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Sludge Oxidation in Limestone FGD Scrubbers

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SLUDGE OXIDATION IN LIMESTONE FGD SCRUBBERS

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16. ABSTRACT

The report gives results of an experimental study of techniques suitable for forcing the oxidation of calcium sulfite (a throwaway product of flue gas desulfurization scrubbers now operating in the U.S.) to gypsum, over a range of scrubber operating conditions applicable to the use of high-sulfur coals. Potential advantages of converting this product to gypsum include: a) reduction of the total waste production, b) improved settling and dewatering properties of the sludge, and c) avoidance of chemical fixation of the sludge. It is shown that appropriate oxidizer designs can achieve complete conversion with reasonable air stoichiometries at atmospheric pressure without catalysts. Gypsum filterable to 80% solids can be obtained in either two- or single-stage scrubbers. In either case, efficiency is determined primarily by the physical absorption of oxygen from the air injected into the oxidizer, when the oxidation step is conducted within the scrubbing loop. The study shows that the required oxygen transfer efficiencies can be obtained either with an air-sparged tower or an with an air ejector, when used to aerate the slurry in the scrubber effluent hold tank. Merits of the various approaches are compared and discussed in terms of the quality of gypsum produced, operability of the system, air-feed pressure requirements, and predictability of performance when scaled-up to larger systems.

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Calcium Inorganic Compounds	Limestone Scrubbers	Stationary Sources	
Gypsum	Wastes	Calcium Sulfite	07B
Oxidation	Sludge	Waste Reduction	08G
Flue Gases	Oxidizers	Chemical Fixation	21B 11G

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SLUDGE OXIDATION IN LIMESTONE FGD SCRUBBERS

by

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ABBREVIATIONS AND SYMBOLS

a	=	specific interfacial area between air bubbles and slurry, m^2/m^3
C	=	O_2 concentration in the bulk liquid phase, g mol/l.
C^*	=	O_2 concentration in the liquid phase at the interface when saturated, g mol/l.
D_b	=	bubble diameter, cm
E	=	O_2 transfer efficiency of oxidiser defined by Equation (5)
EHT	=	scrubber effluent hold tank
h	=	liquid depth in oxidiser during aeration, meters
h_s	=	static liquid depth in oxidiser, meters
H	=	Henry's law constant, meters of water/mol fraction of O_2
K_L	=	overall mass transfer coefficient based on the liquid, m/hr
k_L	=	liquid film coefficient for O_2 diffusion
m_G	=	air injection rate to oxidiser, g mol of air/hr(m^2)
m	=	dry mass of gypsum in EHT, g
M_{SO_2}	=	total SO_2 oxidized in oxidiser, g mol
P	=	absolute pressure, meters water
r	=	relative saturation of gypsum in scrubbing liquor
R	=	1.98 cal/g mol °K
t	=	time, min
T	=	temperature, °K
V	=	volume of slurry in oxidiser, liters
y_0	=	mole fraction O_2 in air feed to oxidiser
y	=	mole fraction O_2 in bubbles leaving oxidiser

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SECTION 1

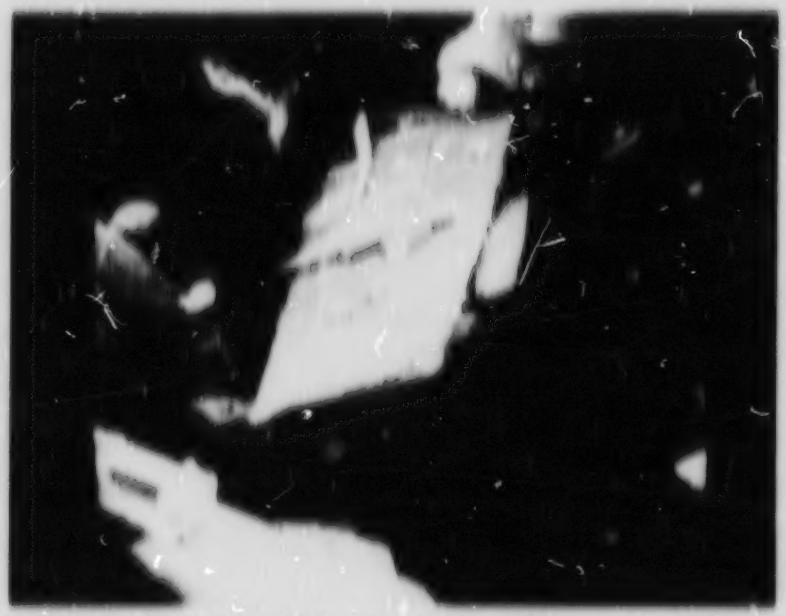
INTRODUCTION

Tests previously reported by EPA[1] showed that calcium sulfite sludge, which is the normal product of limestone Flue Gas Desulfurization (FGD) scrubbers, can be oxidized to gypsum under operating conditions anticipated for scrubbers designed for utilities burning U.S. high-sulfur coals. The EPA tests showed that the two-stage scrubbing approach, which is used in Japan[2], can be modified to permit the oxidation to be carried out within the first-stage scrubbing loop. The first stage pH was controlled at 4.5 in all of those tests, since laboratory investigations of oxidation rate show a maximum at this pH value. The conversion to gypsum was thus accomplished at reasonable air stoichiometries, without addition of catalysts, by air-sparging at atmospheric pressure.

The objectives of forced oxidation are: 1) to improve the settling properties of the slurry (gypsum settles 10 times faster than calcium sulfite and yields a smaller volume of settled sludge); 2) to improve the dewatering characteristics of the sludge (hopefully to the extent that it can be disposed of directly as landfill without chemical fixation); and 3) to reduce the quantity of total waste produced (on the basis of the EPA test results, reductions of 30-40 percent in total waste production should be possible when forced oxidation is combined with dry fly ash collection). As a

practical matter, separate collection of the fly ash appears to be a requirement for achieving all three objectives since the settling properties of the oxidized scrubber slurry can be dominated by fly ash[1]. The improved settling and dewatering characteristics of the oxidized slurry are attributed to the difference in size and shape of the $CaSO_3 \cdot 2H_2O$ and $CaSO_3 \cdot 1/2\ H_2O$ crystals (Figure 1). The larger, thicker gypsum crystals settle faster and form a more compact mass than the smaller flat plates of calcium sulfite.

Although several scrubber designs now offered in the U.S. are adaptable to two-stage operation, most existing systems are not. One objective of the investigations reported here was to determine the feasibility of conducting forced oxidation in single-stage scrubbers, which operate at higher pH's of 5.6 to 6.0. The advantages favoring the production of gypsum as the throw-away product would thus be more widely applicable to present systems without major modification of the scrubber itself. Another purpose of this study was to further explore the variables that influence oxidation efficiency--and thus the amount of air required--with respect to the type of aeration device used, the oxidizer design, and the operating conditions.



A. WITHOUT FORCED OXIDATION: $CaSO_3 \cdot \frac{1}{2}H_2O$ x 2000

B. WITH FORCED OXIDATION: $CaSO_4 \cdot 2H_2O$ x 1000

Figure 1. Comparison of crystals produced in RTP limestone scrubber. (Scanning electron micrographs by Monsanto Research Corp., Dayton, Ohio)

SECTION 2

CONCLUSIONS

A sludge suitable for direct disposal as landfill can be produced from limestone scrubber slurries by forced oxidation to gypsum. This can be accomplished in systems operating with high sulfur coals, with or without chloride.

The total waste produced by a power plant equipped with limestone FGD scrubbers can be reduced by about 45 percent, compared to current practice, if forced oxidation is combined with dry fly ash collection. A final sludge containing 87 percent solids can be thus produced.

The volume of settled scrubber sludge can be reduced about 30 percent by forced oxidation.

Efficient oxidation can be accomplished in either two-stage or single-stage scrubbers. In the former case, the first-stage pH must be controlled below 5 to avoid gypsum scaling. When sufficient particle retention times are provided, gypsum crystals filterable to 80 percent solids and settling at 2 to 3 cm/min can be obtained with either scrubber type. The longer particle retention times characteristic of the single-stage scrubber, together with the neutral pH of the oxidized sludge and the avoidance of pH control, favor the use of single-stage systems.

The oxidation step should be conducted within the scrubbing loop for most efficient oxidation and for best physical properties of the gypsum.

Lime scrubber slurries can be efficiently oxidized in a two-stage scrubber.

The oxidation process is controlled by liquid film diffusion of the O_2 and thus the performance of air-sparged oxidizers is predictable from theory developed for waste water treatment. It should be possible to design full scale FGD oxidizers of this type with confidence.

Oxygen transfer efficiencies of 30 percent were obtained in the pilot plant with a 5.5 m (18 ft) air-sparged tower at 50°C. The transfer efficiency was independent of slurry pH from 4.5 to 6 and independent of the sparger orifice size from 1.6 to 6.4 mm. Air stoichiometries of about 3 will thus be required for complete oxidation in oxidizers of this depth. Higher oxidation towers should yield greater transfer efficiencies and require lower air stoichiometries.

The greatest oxidation efficiency was obtained with an air ejector. The higher O_2 transfer efficiency provided by the ejector will permit the use of lower air stoichiometries and shallower oxidizers than will be possible with spargers. They will also permit the substitution of a slurry pump for an air compressor. The performance of large scale aerators of this type, however, is less predictable than for a sparged tower.

Forced oxidation can be conducted in a single-stage limestone scrubber while meeting the operating conditions required for maximum scrubber relia-

bility; i.e., at limestone utilizations of 85 percent and scrubber feed-liquor supersaturations below 1.3.

SECTION 3

RECOMMENDATIONS

In view of the successful results of the EPA-RTP pilot plant tests with forced oxidation in a single-stage scrubber, and considering the advantages of this mode of operation compared to the two-stage approach, further tests on larger scale equipment are both justified and desirable. The forced oxidation experiments at EPA's Shawnee Test Facility should, if possible, be extended to include single-stage tests as well as those now in progress with the two-stage Venturi/Spray tower. Any such tests should include a larger version of the Penberthy ejector, which performed exceptionally well in the pilot plant, but cannot be scaled up with certainty.

The design of air-sparged towers as oxidizers for FGD scrubbers appears straightforward for systems in which oxidation is conducted within the scrubbing loop. Liquid-film diffusion models that are already available should be directly applicable to this situation when corrected for temperature. The sparger itself should use 6.5 mm orifices to minimize air pressure drop at the injector. Selection of the most economical tower height requires an accurate knowledge of the relationship between the O_2 transfer efficiency and slurry depth; tests of an air-sparged tower at depths greater than 5.5 meters are thus desirable to provide further verification of the diffusion model, at 50°C, for $CaSO_3$ slurries. Tests of this type could most easily be carried out in the RTP pilot plant.

The tests with oxidizer recycle have shown a strong effect on the performance of the sparged tower. It is postulated that countercurrent flow between the rising air bubbles and downward flowing slurry is responsible for the observed increase in efficiency at high recycle rates. If this interpretation is correct, it would permit the effective height of an oxidizer to be increased without penalties of greater pressure for air injection. Thus, the scrubber effluent entering the hold tank/oxidizer might be suitable as a source of downward flow at velocities sufficient to retard the bubbles and prolong contact time. Some carefully controlled measurements of oxygen transfer factors in an air-sparged tower during countercurrent flow would be of potential value.

SECTION 4

THEORETICAL BACKGROUND

In general, the problem of oxidizing the calcium sulfite slurry which is normally produced in limestone FGD scrubbers involves three steps: 1) the dissolution of the solid $CaSO_3$ in order to transfer the SO_2 to the liquid phase of the slurry where the oxidation reaction occurs; 2) the chemical reaction of oxygen and SO_2 in the liquid to produce calcium sulfate; and 3) the absorption of oxygen into the liquid by diffusion from the air that is injected into the oxidiser. The potential limitations of the first step can be avoided by conducting the oxidation within the scrubber loop, which is the procedure used in the tests reported here. In this case, the slurry is continuously recirculated through the low pH region within the SO_2 absorber which accelerates the dissolution of the $CaSO_3$. The other two steps must be taken into account in any attempt to design an efficient oxidiser for FGD systems.

OXIDATION REACTION

The uncatalysed rate of oxidation of calcium sulfite slurries has been accurately measured[3] under conditions at which the chemical reaction is the only resistance. This was accomplished in the laboratory by aerating the reactor with a large excess of air while stirring at high speed, which

minimised the physical resistance imposed by diffusion upon the absorption of oxygen into the liquid. At 50°C and pH 6 this rate is:

$$\text{chemical oxidation rate} = \frac{1}{V}\frac{dH_{SO_2}}{dt} = 1.4 \times 10^{3} \text{ g mol/l.(min)} \quad (1)$$

The chemical oxidation rate increases to a maximum value of 17×10^{13} g mol/l.(min) at pH 4.5, which is the highest rate that can be expected under any circumstances at 50°C; i.e., when there is no diffusion resistance to oxygen absorption.

The first criterion for the design of an oxidiser for FGD systems is that the volume, V (in litres), of the aerated reactor be sufficiently large to satisfy Equation (1) for whatever values of pH and SO_2 feed rate, dH_{SO_2}/dt, one is dealing with. The SO_2 feed rate includes, of course, both the solid $CaSO_3$ and the dissolved SO_2, in g moles per minute.

OXYGEN ABSORPTION

As a practical matter the overall oxidation rate of SO_2 in large equipment is usually controlled, not by the chemical oxidation rate, but by the rate of transfer of oxygen from the air to the liquid. This is because of the slow rate of diffusion of the oxygen through the liquid film which surrounds each bubble and imposes a large resistance to its absorption into the bulk of the liquid where the oxidation reaction occurs. This resistance arises mainly from the fact that oxygen is only very slightly soluble (5.5 mg oxygen per liter of pure water at 50°C, and 1 atm air pressure). Thus, the maximum driving force for diffusion through the liquid film is small. On the basis of pilot plant tests which varied oxidiser depth, it was concluded that oxygen transfer was the predominant resistance to the overall

oxidation rate of calcium sulfite slurries at pH 4.5[1]. Overall rates typically observed in the R/P pilot plant at 50°C ranged from 1.1 x 10^{-3} to 2.7 x 10^{-3} g mol/l. (min) at pH 4.7, well below the 17 x 10^{-3} limit imposed by chemical oxidation rate. This implies that the resistance due to O_2 diffusion is greater than that of the oxidation reaction in solution.

O_2 Transfer Efficiency

The mechanics of oxygen diffusion from an air bubble through the liquid film that surrounds it is depicted in Figure 7, which considers a single bubble rising through a volume of liquid, V. The rate of oxygen transfer from the bubble to the liquid is given by:

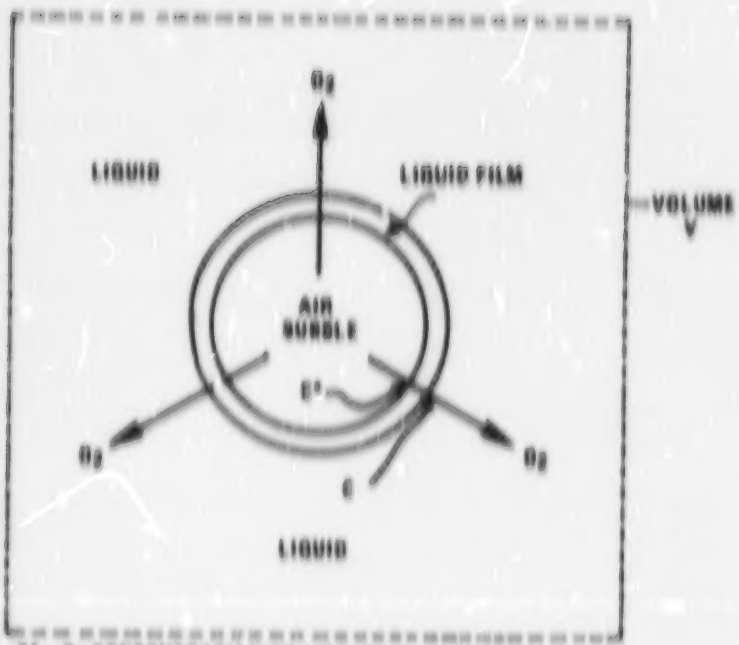
$$\frac{dC}{dt} = K_L a \, (C^* - C) \qquad (2)$$

where C is the concentration of dissolved O_2 in the bulk liquid and C^* is the O_2 concentration at saturation, or limiting solubility. The term a is the surface area of the bubble in contact with the liquid, and K_L is the liquid film transfer coefficient. At steady-state conditions the rate of transfer to a sulfite slurry equals the rate of SO_2 oxidation:

$$K_L a \, (C^* - C) = - \frac{J}{V} \frac{dM_{SO_2}}{dt} \qquad (3)$$

When diffusion controls (i.e., the rate of O_2 transfer through the film is slower than the oxidation rate), the O_2 concentration in the bulk liquid is zero. For this situation, the integrated form of Equation (2) for the air/water system has been shown by Urea and Jackson[4] to be:

$$\frac{E}{1 + 0.791E} + \ln \frac{1 + 0.264E}{1 - E} = \frac{70,000 \, (K_L a) \, h \, (P + h_s/2)}{M_O \, U} \qquad (4)$$



C' = O_2 CONCENTRATION AT AIR/LIQUID INTERFACE

C = O_2 CONCENTRATION IN THE BULK LIQUID

Figure 2. Representation of oxygen diffusion from an air bubble to a liquid, through the liquid film.

where

$$E = \text{oxygen transfer efficiency} = \frac{y_0 - y}{y_0} \qquad (5)$$

and y_0, y are the mole fractions of oxygen in the air feed (= 0.209), and the bubbles leaving the oxidiser, respectively. The term "oxygen transfer efficiency" is widely used in the literature on waste water treatment as a basis for expressing and evaluating the performance of aerated reactors; it is therefore adopted here for the same purpose.

Equation (4) gives the relationship between the oxygen transfer efficiency and the transfer factor, $K_L a$, the air injection rate, m_0, and the total pressure, P, where H is the Henry's Law constant at the temperature of the liquor in the oxidiser, h is the expanded liquor depth in the oxidiser during aeration, and h_s is the static liquor depth in the oxidiser. The value of $K_L a$ has been accurately determined experimentally by Jackson[5] for the transfer of O_2 to sulfite solutions at liquid depths $\leq$ 21.3 meters (Figure 3). Jackson's data were obtained at 20°C for bubbles formed by 6.4-mm sparger orifices, which produced bubbles of 5 mm average diameter.

At a given temperature the value of the transfer factor, $K_L a$, varies directly with the surface area of the bubbles that are in contact with a given volume of liquid. Thus, at a given pressure this area is proportional to the amount of air injection per unit time, m_0, and inversely proportional to the diameter of the bubbles, D_b:

$$K_L a \propto \frac{m_0}{D_b} \qquad (6)$$

The proportional relationship between $K_L a$ and m_0 is tested in Figure 4, using the data of Figure 3. Logarithmic plots of the $K_L a$ values measured by

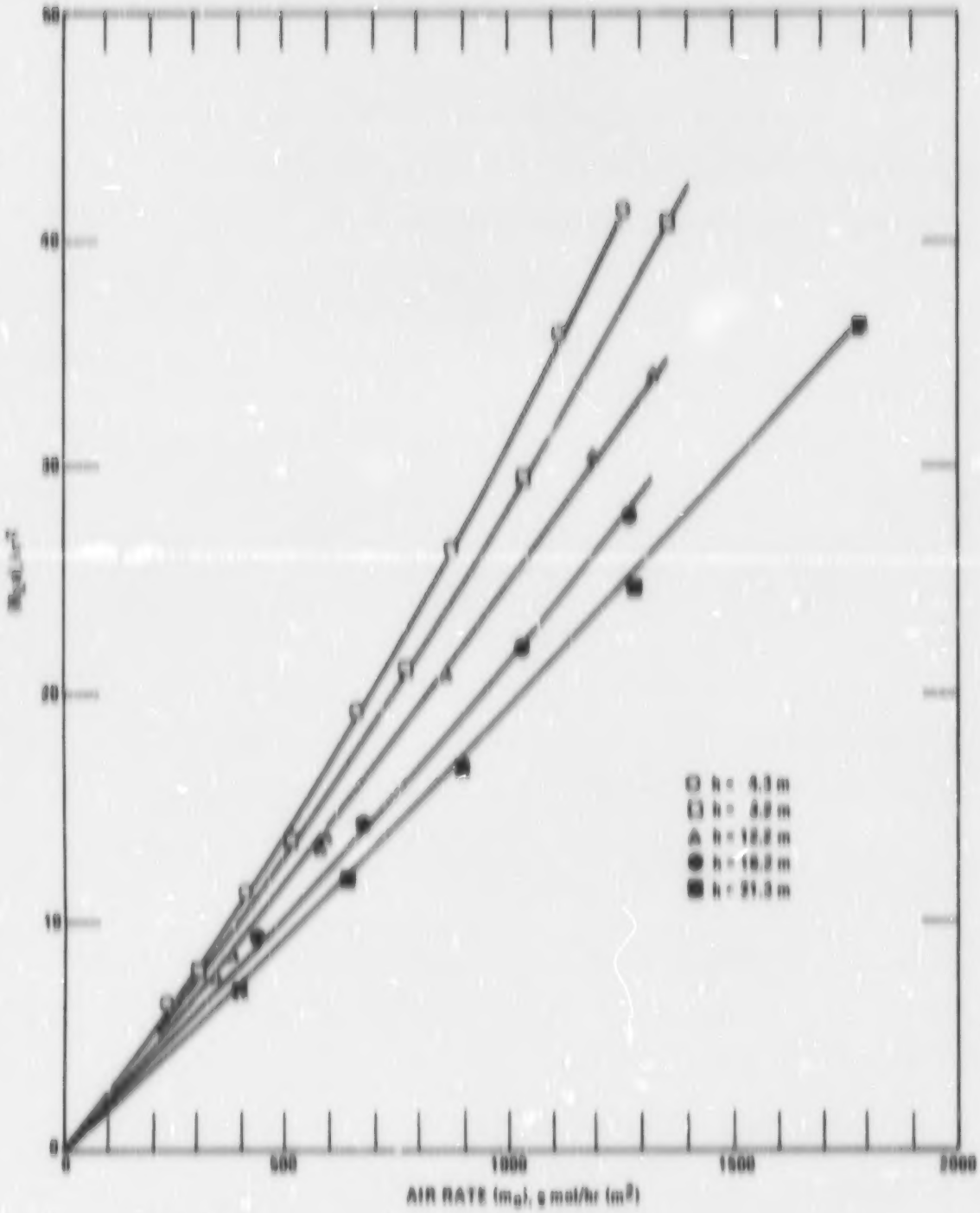


Figure 3. Oxygen transfer factor as a function of liquid depth and air injection rate in air sparged towers. Data of Jackson[5] at 20°C.

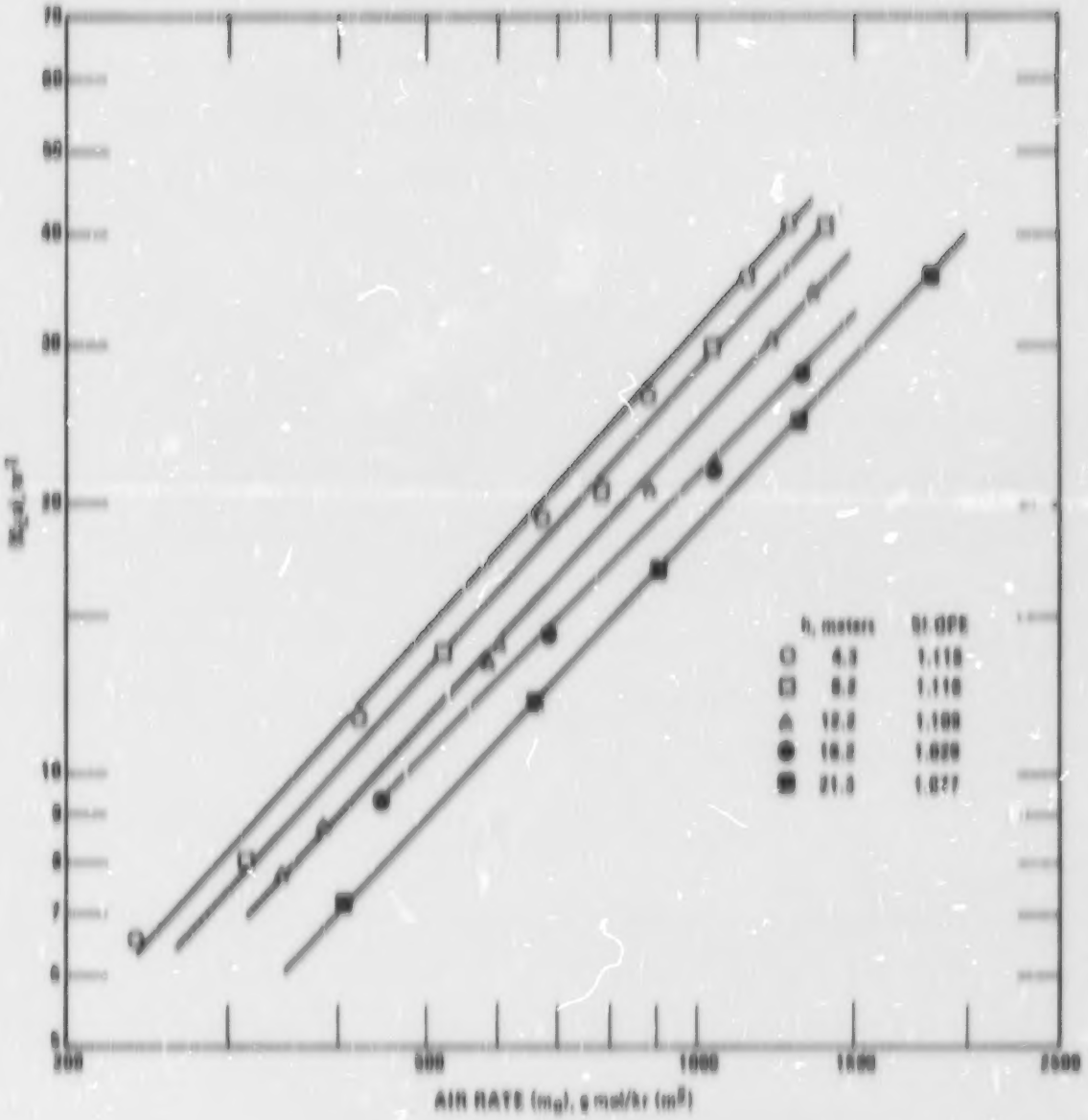


Figure 4. Effect of air injection rate on the oxygen transfer factor at constant pressure. Data of Figure 3, 20°C.

Jackson are shown as a function of the logarithm of the air injection rate at each of five different constant pressure conditions (tower heights). It is evident from Figure 4 that K_La increases slightly faster than a linear function of air rate; the average slope is 1.09 rather than the 1.00 expected from Equation (6). The difference indicates that some breakage of the bubbles occurs at the higher injection rates, producing additional surface area.

Pressure also influences the transfer factor. As the tower height is increased, the average ambient pressure of the liquid upon the bubbles increases, thus reducing their size and total area. If the density of the bubbles at the point of formation remains constant as the pressure is increased, then the total surface area would decrease with the two-thirds power of the ambient pressure. Figure 5 shows the effect of pressure on K_La, again based on Jackson's data of Figure 3, at a constant air injection rate. The average K_La decreases in direct proportion to the average pressure as the tower height is increased. The pressure plotted in Figure 5 is:

$$\text{Average absolute pressure} = P + h_s/2$$

where P is the atmospheric pressure, in meters of water, and h_s is the static liquid depth in the oxidizer above the sparger, also in meters of water. Most of this pressure effect is accounted for by the change in volume of the air, and thus the interfacial surface area. It is also evident that the density of the bubbles formed at high pressure is significantly greater than the density of bubbles formed at lower pressure.

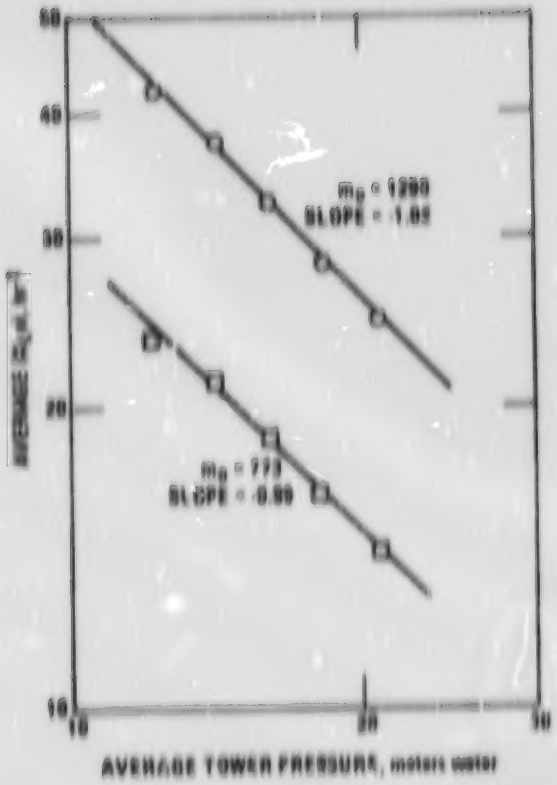


Figure 6. Effect of pressure on the oxygen transfer factor at constant air injection rate. Data of Figure 5, 20°C.

It follows from Figures 4 and 5 that the transfer factor for a sparged tower (at 20°C) can be expressed empirically as:

$$K_L a = 0.214 \frac{m_g^{1.09}}{P + h_s/2} \qquad (7)$$

The accuracy of Equation (7) in correlating Jackson's data is shown in Figure 6.

From Equations (4) and (7) it is evident that the O_2 transfer efficiency is, for practical purposes, a function only of the liquid depth for bubble residence time in the oxidizer) at any given temperature.

Temperature affects the oxygen transfer efficiency in two ways: 1) as temperature increases, the solubility of O_2--and thus the value of H in Equation (4)--is reduced; and 2) the transfer coefficient for liquid film diffusion is increased. The magnitude of each of these effects is known. At a normal FGD scrubber temperature (and therefore, oxidizer temperature) of 50°C, H = 7 x 10^5 meters water per mole fraction. The value of $K_L a$ can be estimated from Equation (7) and the data of Sherwood and Pigford[6]:

$$K_L a \text{ @ } 50°C = 2.08\ K_L a \text{ @ } 20°C$$

$$\text{and } a \text{ @ } 50°C = \left(\frac{293}{323}\right)^{-2/3} a \text{ @ } 20°C$$

$$\text{Therefore, } K_L a = 2.08 \left(\frac{293}{323}\right)^{-2/3} \frac{0.214\ m_g^{1.09}}{P + h_s/2} \qquad (8)$$

With Equations (8) and (4) the oxygen transfer efficiency at 50°C can be represented by:

$$\frac{E}{1 + 0.791E} + \ln \frac{1 + 0.264E}{1 - E} = 0.0474\ m_g^{0.09}\ h \qquad (9)$$

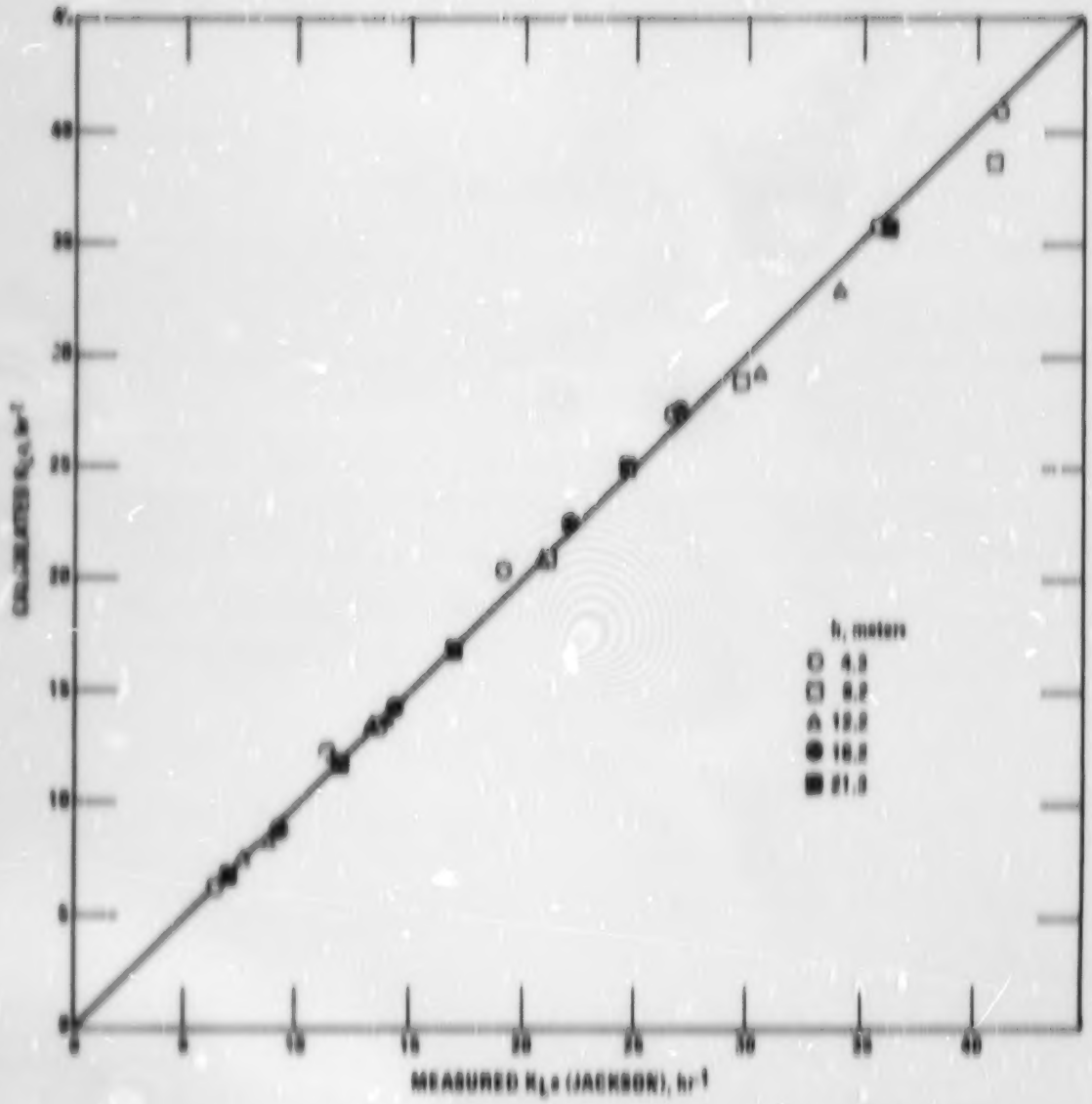


Figure 6. Oxygen transfer factors for air-sparged towers at 20°C. Test of Equation (7) with data of Figure 3.

Equation (9) is plotted in Figure 7 over the range of air injection rates used in the RTP pilot plant. It shows the relationship between oxidiser height and the oxygen transfer efficiency expected when calcium sulfite slurries are air-sparged at 50°C. The correlation includes the effect of m_o on the height of the slurry in the oxidation tower, which expands by 1 and 3 percent, respectively, at m_o = 1000 and m_o = 3000 g mol/hr(m^2). The transfer efficiencies shown in Figure 7 are about 20 percent greater than those calculated at 20°C. The net effect of higher temperature is thus to increase the O_2 transfer, a result brought about by the relatively large reduction in film resistance compared to the change in oxygen solubility.

Air Stoichiometry

Equation (9) can be used to estimate the minimum air requirement for complete oxidation in a given oxidiser configuration when liquid film diffusion controls. The minimum air requirement is defined by an air stoichiometry of 1.0, where

$$\text{Air stoichiometry} = \frac{\text{g atoms of } O_2 \text{ injected as air}}{\text{g moles of } SO_2 \text{ absorbed in scrubber}} \qquad (10)$$

$$= \frac{(\text{kg/hr air fed})\ 0.21\ (64.1)\ 2}{29\ (\text{kg/hr } SO_2 \text{ absorbed})}$$

Equations (5) and (10) show that the air stoichiometry and oxygen transfer efficiency are related by:

$$\text{Air stoichiometry} = \frac{\text{oxidation in oxidiser}}{O_2 \text{ transfer efficiency}} \qquad (11)$$

where the numerator in Equation (11) is the moles of SO_2 oxidised in the oxidiser per mole SO_2 absorbed in the scrubber. Generally, 15-25 percent of the SO_2 absorbed is oxidised in the scrubber, which reduces the amount

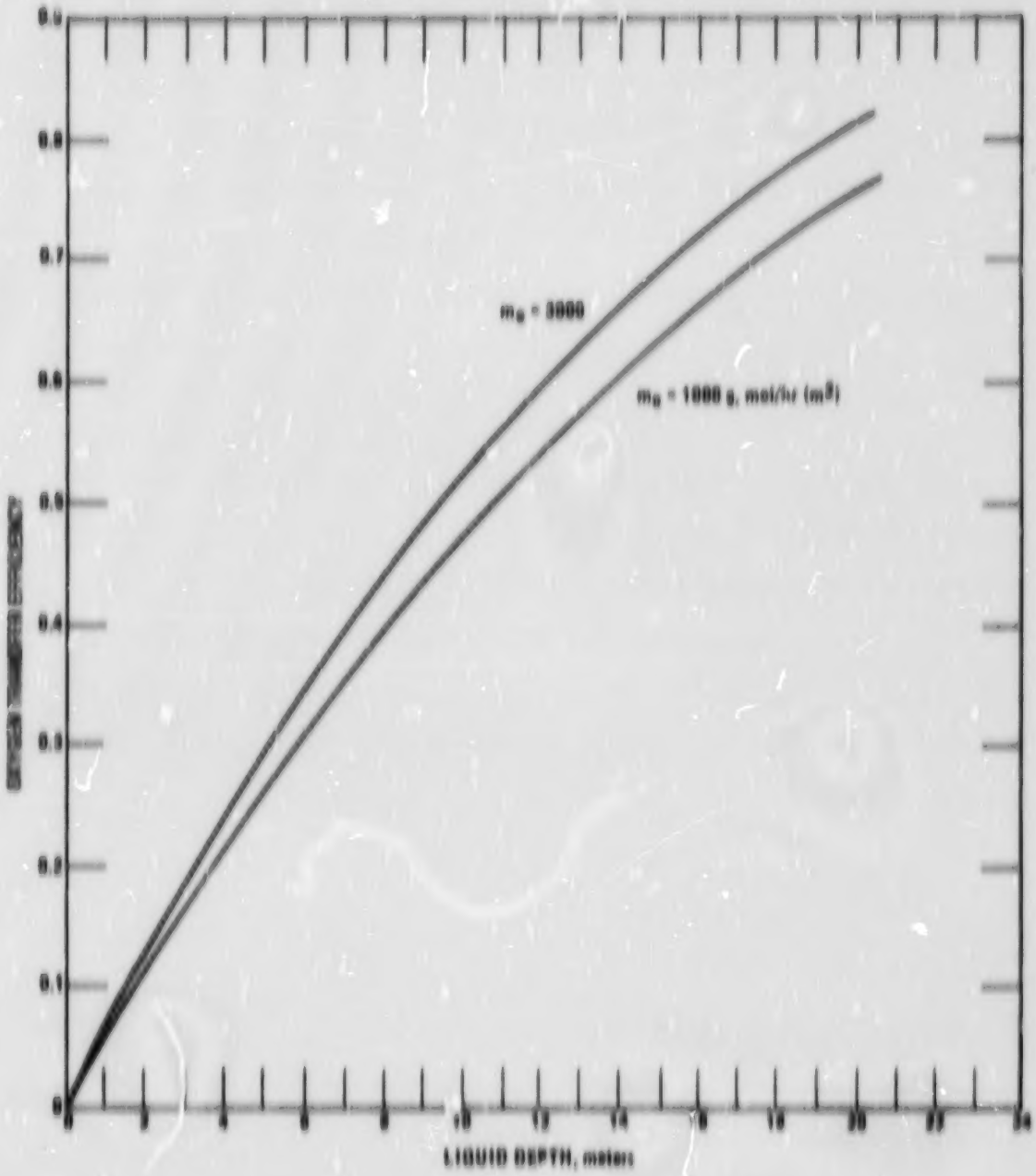


Figure 7. Oxygen transfer efficiency at 60°C, as a function of liquid depth. Curves calculated by Equation (9).

of oxygen that must be transferred in the oxidizer. In the experiments reported here, the oxidation in the oxidizer was determined as:

Oxidation in oxidizer =

Final oxidation of sludge - Oxidation in scrubber

In those situations where the scrubber oxidation could not be separately determined, such as the experiments with single-stage scrubbers, the tests were made under conditions which limited the scrubber oxidation to only about 15 percent of the SO_2 absorbed and this value was assumed in using Equations (10) and (11).

For reasons of operating economy, especially in terms of the power requirements for air compression, the oxidizer must be operated at an air stoichiometry as close to 1.0 as practicable. Equations (9)-(11) provide a basis for oxidizer design where the physical absorption of O_2 is the controlling factor. In the following description of the pilot plant tests maximum effort is made to evaluate and interpret the results in terms of these relationships.

SECTION 5

PROCEDURE

EQUIPMENT

The FGD pilot plant operated by EPA's Industrial Environmental Research Laboratory at Research Triangle Park (RTP), N.C., consists of two scrubbers, each 23 cm diam. x 3 m high and each having a flue gas capacity of 8.5 m^3/min. They are operated for the purpose of providing in-house experimental support for EPA's larger prototype-scrubber test facility at TVA's Shawnee power plant in Paducah, KY. The RTP scrubbers are 1/100 the capacity of the Shawnee prototypes and 1/1000 full scale.

Two-stage scrubbing experiments were conducted with the two towers connected in series so that the hot flue gas entered the "first stage," and then passed into the "second stage," which was the principal SO_2 absorber. The limestone feed entered the second stage, from which the partially reacted slurry was then fed to the first stage so that flue gas and slurry flows were countercurrent through the two scrubbers. Each stage contained its own scrubber effluent hold tank (EHT) and slurry recirculation pump. The first-stage SO_2 absorber was always operated as a spray tower at L/G = 2.7 $l./m^3$. The second stage was operated at L/G = 9.3 $l./m^3$, either as a spray tower or as a turbulent contact absorber (TCA). The second-stage EHT was initially set up with three tanks in series with 9 min total residence time; later

tests were made with a single 9-gal stirred tank. The first-stage EHT consisted of an air-sparged tower, containing slurry of variable depth, which operated in series with a 163-liter stirred tank. The tank served to increase the particle retention time* for growth of the gypsum crystals. The pH was manually controlled in the first stage by means of the rate of limestone feed to the second stage.

Tests conducted with a single-stage scrubber were made in the TCA configuration, with three 13-cm beds of 3.8-cm diam (5 g) spheres and 2.7 m/sec gas velocity at L/G = 9 to 11 $l./m^3$. The EHT volume was 718 liters, providing a residence time of 10 minutes. This tank was aerated by either of two methods: an air-sparged tower or an air ejector. In the latter case, a single stirred (1725 rpm) tank was used which had a slurry depth of 1.1 meters. When the sparged tower was used for aeration, it consisted of a 30.5-cm diam PVC pipe containing 400 liters of slurry at a depth of 5.5 meters; this tower was followed in series by a 318 liter stirred tank from which the slurry was pumped back to the scrubber.

The following operating conditions applied to both two-stage and single-stage testing: inlet SO_2 concentration in the flue gas = 2700 to 3000 ppm, inlet O_2 concentration in the flue gas = 4 to 6 percent, chloride concentration in the scrubbing liquor = 3000 to 5000 ppm (added as HCl gas to the flue gas entering the scrubber), oxidizer temperature = 50°C, and scrubber slurry = 8 percent solids without fly ash. The sludge was dewatered in a rotary vacuum filter, 91 cm diam x 61 cm wide, with all filtrate returned to the scrubber.

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*Particle retention time = EHT volume (l.)/slurry purge rate (l./hr)

APPROACH

The oxidizer was set up in a manner that permitted the oxidation reaction to be conducted within the scrubbing loop. With only one exception, the tests were made without catalyst addition. Since the scrubber towers were glass-walled and the oxidizer, EHT, and connecting piping were all plastic, the slurry was not in contact with catalytic surfaces; any catalyst that may have been present could only have entered the system as an impurity in the limestone. The limestone used in all tests was obtained from EPA's Shawnee Test Facility; its composition was 90 percent $CaCO_3$, 2 percent $MgCO_3$, and 2 percent insoluble inerts.

The goal of the test program was to improve the dewatering properties of the sludge by means of forced oxidation. The two-stage system, which had already been successfully tested, was used in the current experiments to obtain information concerning the effects of pH as an operating variable. On the basis of experience gained with the two-stage system, the tests were extended to a single-stage scrubber. Another objective, therefore, was to establish suitable scrubbing configurations and operating conditions for applying forced oxidation to all types of scrubbers that will be operating at power plants in the U.S., and especially those burning high sulfur coal. The earlier RTP tests showed that complete oxidation of the slurry (at least 90 percent) is required to obtain good sludge properties. The tests reported here, therefore, had the additional objective of finding an efficient method of oxidising the slurry while using the minimum amount of air. Various oxidation schemes were tested in a manner that permitted estimation of the minimum air stoichiometry required for complete oxidation.

The oxygen transfer efficiency, defined in Section 4, is used as the basis for estimating the minimum air stoichiometry required for complete oxidation and for comparing the performance of oxidisers. The oxygen transfer efficiency must be measured at operating conditions which yield incomplete oxidation of the calcium sulfite; thus some tests are reported in which the air injection rate was deliberately limited below the minimum stoichiometry. This approach avoids many trial and error tests that would otherwise be necessary.

SECTION 6

RESULTS

TWO-STAGE SCRUBBING

A two-stage scrubber is defined here as a system containing two absorbers in series, each absorber with its own EHT. Figure 8 illustrates one type of two-stage system tested at RTP. Although the first stage consisted of a spray tower in all RTP experiments, a venturi can also be used for the first stage. Fresh limestone is fed to the second stage where most of the SO_2 absorption occurs and about 80 percent of the limestone is reacted. The partially reacted slurry is then fed to the first stage where additional SO_2 absorption occurs, lowering the pH and further increasing the limestone utilization. The main advantage of this system, as far as forced oxidation is concerned, is that it permits the two stages to operate at different pH values. Thus, the first stage pH can be controlled at low values for maximum oxidation efficiency, while the second stage operates at the higher pH's needed for most efficient SO_2 absorption. This arrangement also maximizes the utilization of the limestone, which averaged 95 percent in the RTP tests.

Forced oxidation testing was begun at RTP using the two-stage--rather than a single-stage--system because the greatest possibility of success could be expected at low pH, where the $CaSO_3$ solubility and the

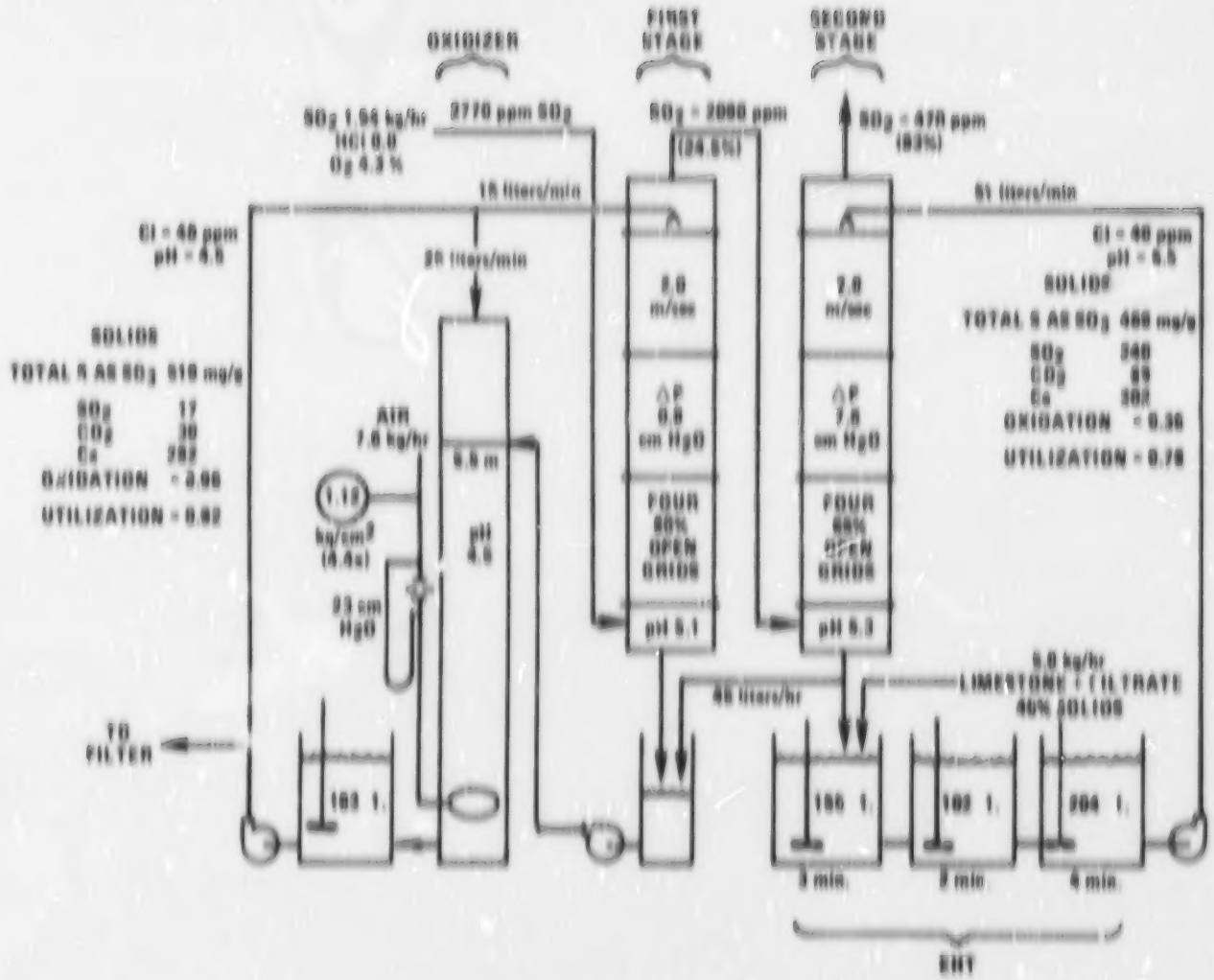

Figure 8. Two-stage limestone scrubbing with forced oxidation in the first stage.

overall rate of oxidation are greatest. From the experimental standpoint, the two-stage system is the preferred starting point even though it is somewhat more complicated, operationally, than a single-stage system. The initial results with the two-stage system were reported[1] at the New Orleans FGD symposium (March 1976) and showed that complete oxidation could be obtained at air stoichiometries of 6-7 when a shallow (h = 0.9m) tank was used as a combination oxidizer/RHT in the first-stage scrubbing loop. By substituting a tower (h = 5.5m) for the stirred tank, as shown in Figure 8, complete oxidation was obtained at air stoichiometries as low as 2.3. Aeration was provided in both systems by a sparger containing 22, 1.6 mm orifices. The improvement in oxidation efficiency brought about by increasing the oxidizer height was attributed to the greater contact time between the air bubbles and the slurry. This result, which is in accordance with the effects described by Equation (8), was evidence that oxygen transfer was controlling the performance at pH 4.5.

Recycle

The importance of air/liquid contact time was further evidenced by experiments recently completed at RTP, in which the slurry recycle to the oxidizer was discontinued. This recycle, indicated in Figure 8 by an arrow entering the top of the oxidizer, was provided for the purpose of mixing the slurry to prevent settling of solids inside the oxidizer. At normal recycle rate the slurry moved downward through the 20-cm diameter tower at 340 cm/min. Tests without recycle showed that it had a significant effect on oxidation efficiency, air stoichiometries of 3 being necessary for complete oxidation at pH 4.5. The observed effect of recycle on oxidation efficiency can

be explained in terms of O_2 transfer efficiency: the countercurrent flow imposed by recycle retarded the rising air bubbles and increased the contact time; the effective height of the tower was increased as a net result of the recycle.

The 103-L tank shown in the first stage loop of Figure 8 was added to provide additional residence time for the growth of gypsum crystals during the oxidation process. This tank increased the residence time from 7 min to 18 min, based on the slurry recirculation rate, and resulted in a general improvement in settled density and filterability of the oxidized sludge. The gypsum thus produced settled at a rate of 3 cm/min, to a final density of 1 gram (dry solids) per ml, and filtered to a sludge containing 75 to 80 percent solids.

Oxidizer pH

The principal objective of the pilot plant tests reported in this section was to evaluate the importance of pH as a variable influencing the efficiency of forced oxidation, particularly in terms of the amount of air required. To put this question in perspective, the two-stage scrubbing approach was adopted for the initial Kiln oxidation experiments on the assumption that low pH is a necessary condition for efficient oxidation. Numerous laboratory investigations have shown that the oxidation rate of $CaSO_3$ slurries increases as pH is reduced from 7 to 4.5. If the rate of chemical oxidation in solution is the controlling factor, then two-stage operation at low oxidizer pH should provide an advantage. If, as the discussion above implies, the O_2 transfer from the air to the liquid is controlling, then pH would be important only at values greater than that pH at which chemical reaction rate equals the O_2 transfer rate.

The first direct indication that low pH may not be a crucial factor for forced oxidation occurred during experiments aimed at evaluating the effect of slurry "carry-over." These tests simulated the entrainment of 20 percent of the first-stage feed liquor into the gas stream. Since the transfer of this slurry to the second stage must be accompanied by an equal amount of slurry fed forward from the second stage to the first, the pH is equalized in the two stages. Despite the higher pH in the oxidizer during the carry-over tests (pH = 5.0-5.5) complete oxidation was still obtained. This result prompted further tests intended specifically to determine the effect of the first stage pH on oxidation efficiency. They were conducted with zero carry-over, increasing the first stage pH by operating the system at higher limestone feed stoichiometry. The scrubber configuration was that shown in Figure 8.

The ensuing tests at high limestone stoichiometry showed two important results: 1) the overall SO_2 removal efficiency was significantly improved by increasing the first stage pH--operating with two spray towers in series at an overall pressure drop of 8 cm water, 85 percent average SO_2 removal was obtained with a first stage pH of 6 compared to 76 percent average removal at pH 4.5; and 2) the first stage tower consistently scaled with gypsum when operated at pH's greater than 5--controlling the first stage pH below 5 was a necessary condition for avoiding scaling in the RTP scrubber. The scale formed on the grids and glass walls, mostly in the upper third of the tower around the slurry feed nozzle.

It was apparent that the greater SO_2 removal efficiency that could potentially be obtained in the two-stage system by operating at high lime-

stoich. stoichiometry could not be realised in practice because of the scaling problem. As far as the effect of pH on the oxidation efficiency was concerned, the results of these experiments were similar to the carryover tests: oxidation could still be completed at high limestone stoichiometry and oxidiser pH's as high as 6.5.

The final test with the two-stage scrubber made a direct comparison of the effect of pH on oxidation efficiency. The recycle to the oxidation tower was cut off and the air stoichiometry set at 3.0 with an oxidiser height of 3.2 meters. At these conditions, 68 percent oxidation was obtained at pH 4.5, and 36 percent oxidation was obtained when the pH was increased to 6. The difference in oxidation rates over this extreme range of pH was insignificant compared to the difference between the corresponding uncatalysed chemical reaction rates: 17×10^{-3} g mol/l.(min) at pH 4.5 vs. 1.4×10^{-3} at pH 6. Figure 9 summarises the operating conditions of the test at pH 4.5; the oxidation rate was far slower than would be expected if chemical reaction were limiting:

$$\text{oxidation rate} = \frac{1900(0.83)(1 - 0.245)0.68}{102(60)64.1} = 2.1 \times 10^{-3} \text{ g mol/l.(min)}.$$

It is therefore evident that oxygen transfer, rather than the oxidation reaction, was controlling. Since Equations (9)-(11) apply in this case:

$$\underset{(h = 3.2m)}{\text{oxygen transfer efficiency}} = \frac{\text{oxidation in oxidiser}}{\text{air stoichiometry}}$$

$$= \frac{0.68 - 0.245}{3} = 0.145$$

The minimum air stoichiometry required for complete oxidation with an oxidiser height of 5.5 meters* would be:

*Transfer efficiency is taken to be directly proportional to oxidiser height for h<6 meters, per Figure 7.

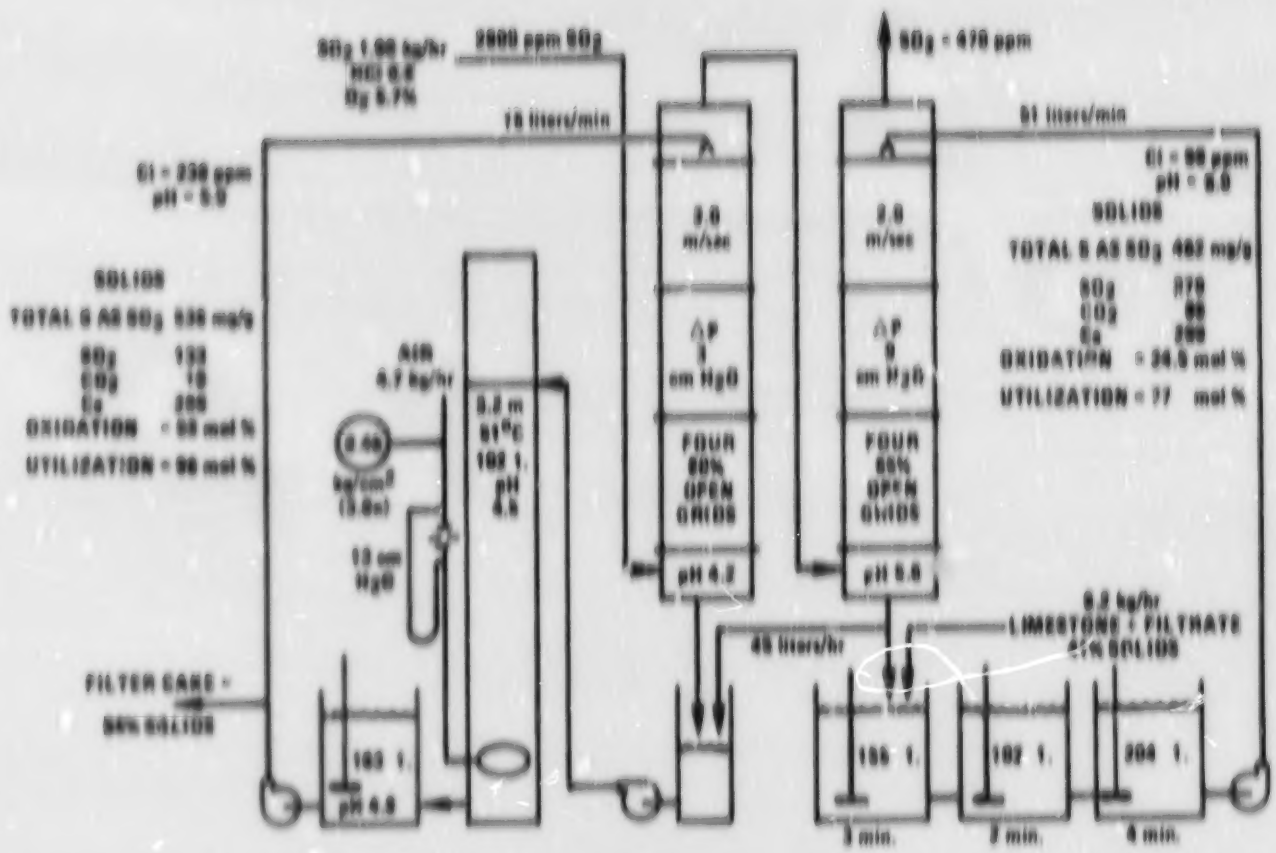

Figure 9. Pilot plant test conditions for estimating oxygen transfer efficiency at pH 4.5, h = 3.2 m.

$$\underset{(h = 5.5m)}{\text{air stoichiometry}} = \frac{(1 - 0.245)\ 3.2}{0.145 \times 5.5} = 3.0$$

Another test, similar to the one above, was conducted at pH 6 with $MnSO_4$ catalyst added to provide a concentration of 40 ppm Mn^{++} in the oxidiser liquor. If the chemical reaction rate were limiting, the test would be expected to show an acceleration of the rate of oxidation relative to the uncatalysed value of 1.4×10^{-3} g mol/l.(min). Operating at 5.5 meters oxidiser height and without recycle, the observed rate was 1.3×10^{-3} g mol/l.(min), the same as the uncatalysed value. The test verified that oxygen transfer was also limiting at pH 6, since the overall rate was not influenced by catalysis. The test was conducted at an air stoichiometry of 1.7, at which the final oxidation was 62 percent and the initial (scrubber) oxidation was 12 percent. Thus, the

$$\underset{(h = 5.5m)}{\text{oxygen transfer efficiency}} = \frac{0.62 - 0.12}{1.7} = 0.29.$$

The estimated minimum air stoichiometry required for complete oxidation is:

$$\underset{(h = 5.5m)}{\text{air stoichiometry}} = \frac{1.0 - 0.12}{0.29} = 3.0.$$

It is concluded from these tests that the effect of pH (more specifically, the effect of the chemical oxidation reaction in solution) is insignificant compared to the effect of oxygen transfer on the overall rate of SO_2 oxidation in the pilot plant at pH levels up to at least 6.

Lime Feed

The two-stage scrubber was operated successfully with lime feed at the conditions shown in Figure 10. The pH in the first stage was controlled manually at 4.5, which yielded an average pH of 7.5 in the second-stage

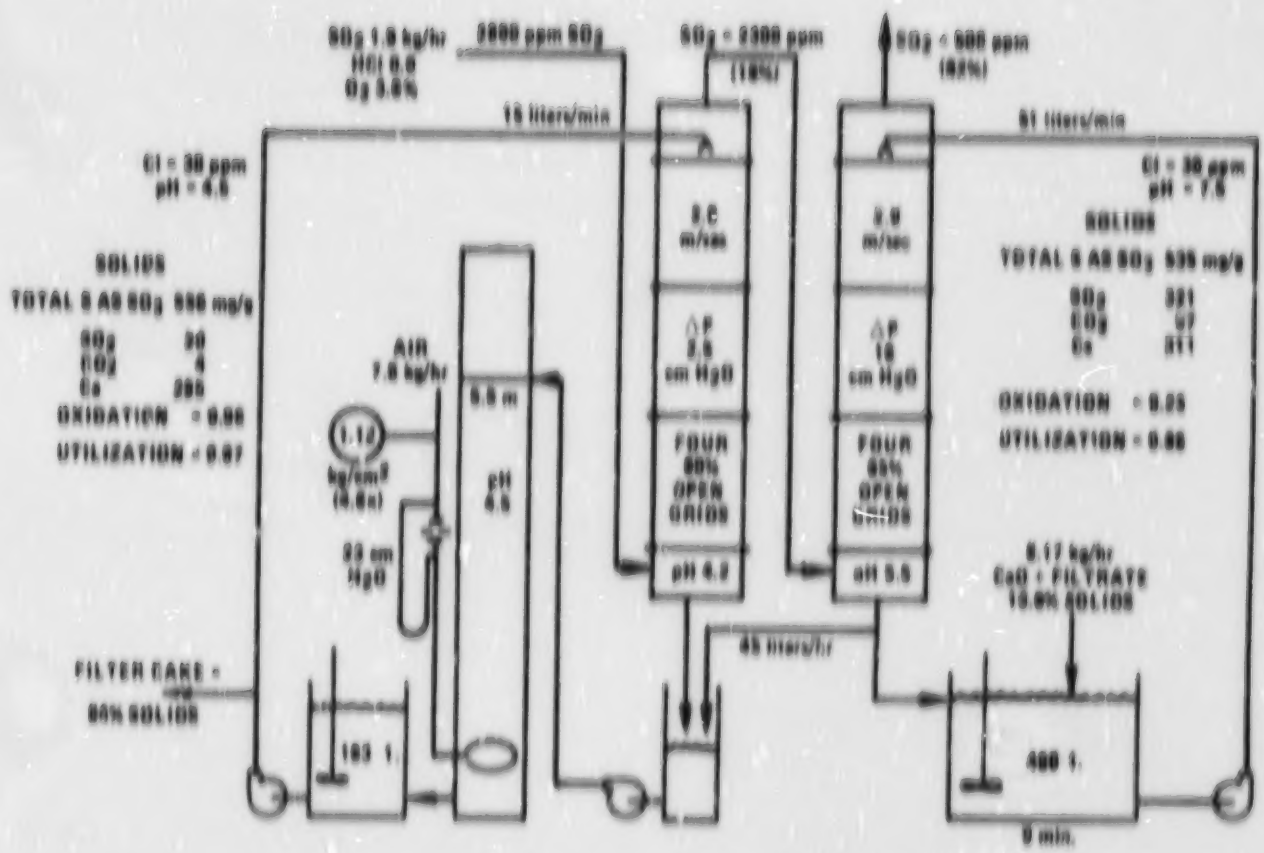

Figure 10. Two-stage scrubbing with lime feed, no oxidizer recycle.

scrubber. Automatic control based on a second-stage pH of 7.5 may be feasible; however, an attempt to operate the RTP scrubber on automatic control at pH 8 resulted in the same pH in both stages with poor oxidation and severe first-stage scaling. It is clear that the second stage pH must be kept below 8; when this is done, good oxidation can be obtained in the first stage to produce gypsum of excellent settling and dewatering properties.

Chloride

An example of a run made with no chloride is shown in Figure 8. It was previously shown that forced oxidation can be conducted at the normal chloride levels of 3000-5000 ppm expected at Shawnee[1], and most of the RTP testing was conducted within this range. A test at very high chloride is shown in Figure 11. No adverse effect on oxidation efficiency was evident with 14,000 ppm chloride in the oxidizer liquor.

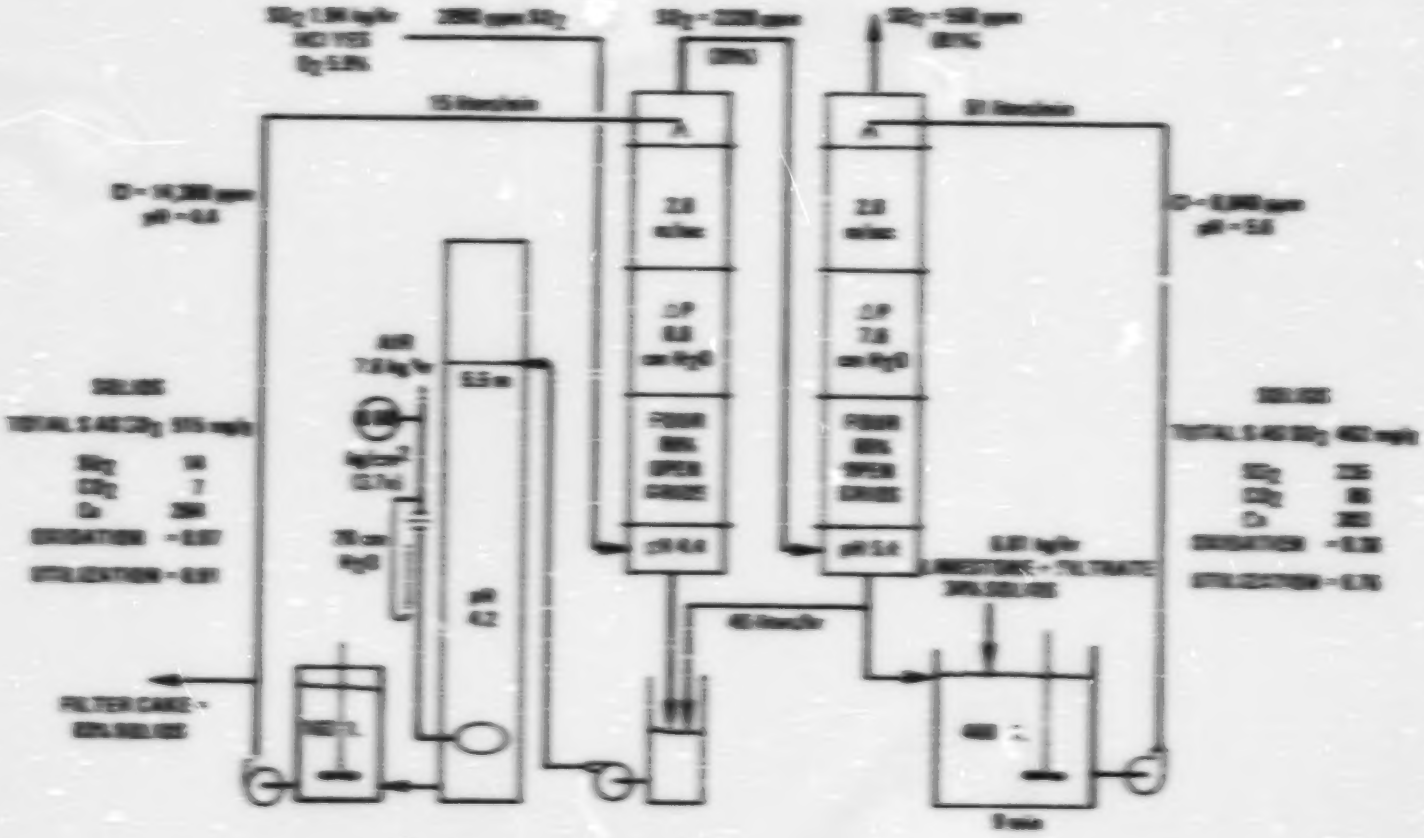

Figure 11. Forced oxidation test at high chloride concentration.

SINGLE-STAGE SCRUBBING

The importance of the pH question, as addressed in the two-stage oxidation experiments described in the previous section, has to do with the prospects for applying forced oxidation to single-stage scrubbers. That prospect is clearly unfavorable if pH 4.5 is required. The situation is different, however, if oxidation can be carried out at pH 6 which is within the range of normal operation of single-stage limestone scrubbers.

As indicated in Section 4, laboratory measurements of the uncatalyzed oxidation rate of $CaSO_3$ slurries are reported to be 1.4×10^{-3} g mol/l.(min) at pH 6 and 50°C. The two-stage scrubbing experiments at RTP confirmed that oxidation rates of at least this magnitude can be sustained in an uncatalyzed scrubber under actual operating conditions. If the constraint specified by Equation (i) can be satisfied with respect to oxidizer volume in a single-stage scrubber operating at pH 6, then it should be possible to force the oxidation to completion as long as sufficient oxygen transfer efficiency is provided. The simplest approach to providing the oxygen transfer would be to aerate the scrubber effluent hold tank (EHT). In this situation Equation (i) demands that the EHT have sufficient volume so that the SO_2 feed rate does not exceed 1.4×10^{-3} g mol/l.(min).

Typical operating conditions for a single-stage limestone scrubber are shown in Figure 12, based on operating experience at the EPA/Shawnee Test Facility. The SO_2 absorbed in the scrubber and fed to the EHT is:

$$580{,}000\ (1-0.08)\ 0.90\ (0.003)\ \frac{273}{423}\ \frac{1}{22.4} = 41.5 \text{ g mol/min.}$$

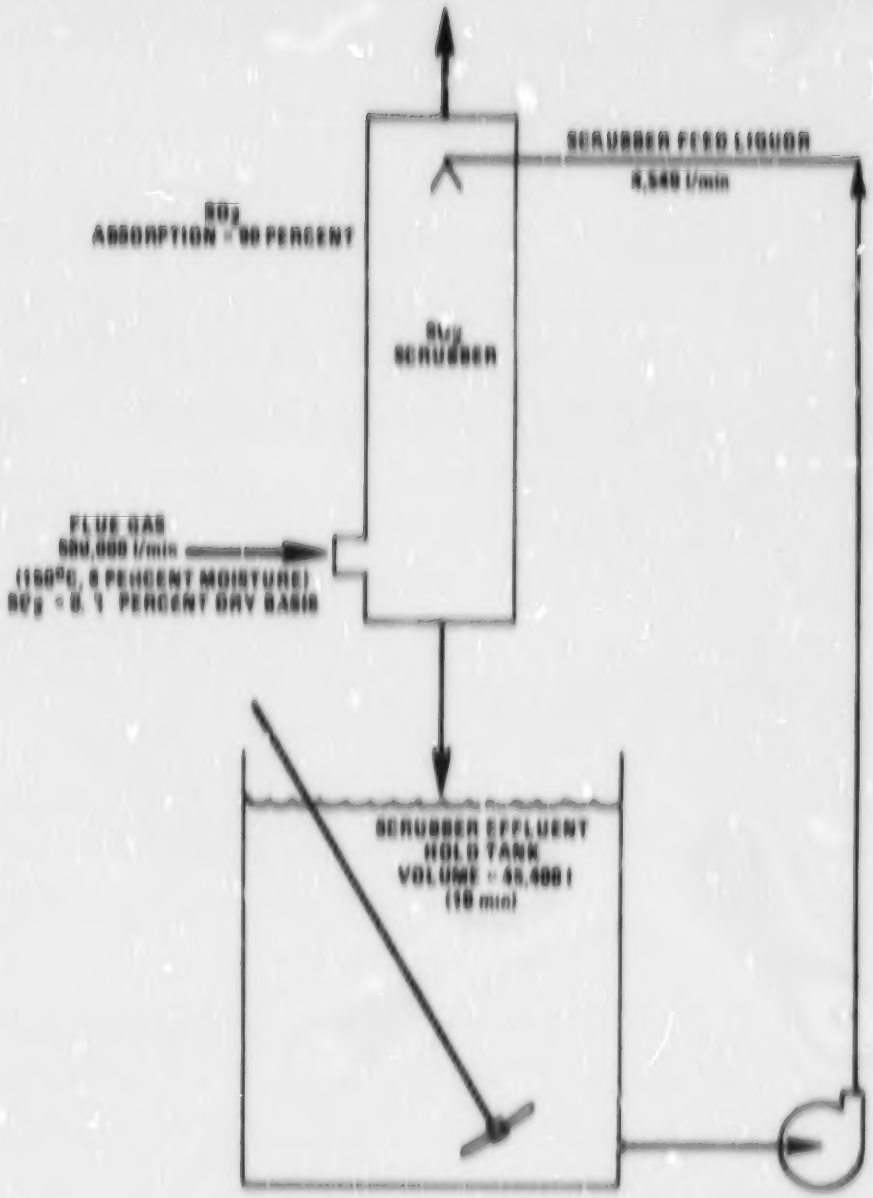

Figure 12. Typical operating conditions for single-stage lime-stone scrubber at Shawnee Test Facility.

With a 10-min EHT residence time, the maximum oxidation rate required for complete conversion of this amount of HO_3^- is:

$$\text{oxidation (EHT feed) rate} = \frac{41.3}{43400} = 0.91 \times 10^{-3} \text{ g mol/l.(min)}$$

Since this rate is less than the rate observed at pH 6, both in the laboratory and in the RTP scrubber, the oxidation efficiency in a single stage system of this type should be a function only of the O_2 transfer efficiency in the aerated EHT. As far as the chemical oxidation rate is concerned, Equation (1) will be satisfied for the system shown in Figure 12 at EHT residence times as short as 6-1/2 minutes, even if no oxidation occurs in the scrubber itself and no catalysts are added. The experiments reported in this section were carried out to determine if oxidation can be forced to completion in a single-stage system under realistic operating conditions when good oxygen transfer efficiency is provided.

Air-Sparging Tests

Figure 13 summarizes a single-stage scrubbing test in which the EHT was aerated at a slurry depth of 5.5 meters (oxidizer area = 0.0729 m^2) which, as previously shown, has an oxygen transfer efficiency of 0.29. A second stirred tank was added, as shown in the figure, to provide a total residence time of 10 minutes. The oxidation tower was sparged with air at a rate of m_g = 3260 g mol/hr(m^2) using 22 orifices of 1.6 mm diameter. As shown by the results in Figure 13, 97 percent oxidation was obtained at an air stoichiometry of 2.9 while operating at a limestone stoichiometry of 1.3 (pH = 6.1). The oxidation rate was:

$$\text{oxidation rate} = \frac{2670\ (0.83)\ 0.97}{64.1\ (60)\ 400} = 1.6 \times 10^{-3} \text{ g mol/l.(min)}$$

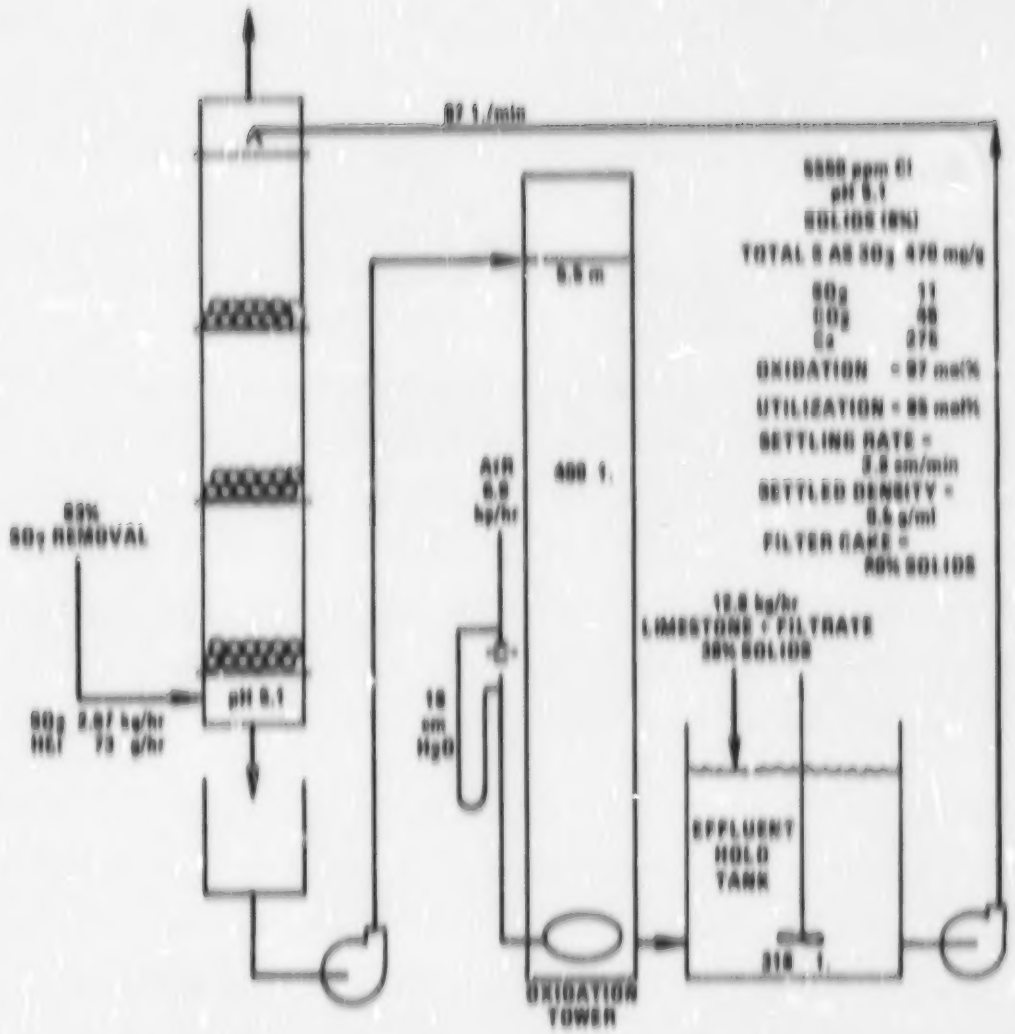

Figure 13. Pilot plant simulation of single-stage scrubbing with forced oxidation in the scrubbing loop; pH = 5.1, air stoichiometry = 2.0.

For an accurate estimate of the oxygen transfer efficiency, another run was made at a lower air stoichiometry of 2.2 at which the oxidation was incomplete. The air injection rate in this run was 2370 g mol/hr(m^2) which yielded 75 percent final oxidation. Assuming 15 percent oxidation in the scrubber, the oxygen transfer efficiency is:

$$\underset{(h = 5.5\ m)}{\text{oxygen transfer efficiency}} = \frac{0.75 - 0.15}{2.2} = 0.27.$$

The air stoichiometry required for complete oxidation, which agrees well with the values previously obtained with the two-stage scrubber, is:

$$\text{air stoichiometry} = \frac{1.0 - 0.15}{0.27} = 3.1$$

It is concluded that oxidation can be forced to completion at reasonable air stoichiometries in a single-stage scrubber operating at normal limestone stoichiometry. In accordance with Equation (9) one could expect oxygen transfer efficiencies greater than 0.27 if the EHT were designed with a slurry depth greater than 5.5 meters. For example, a tank with a slurry depth of 10 meters (33 ft) would provide an oxygen efficiency of 0.5, requiring an air stoichiometry of only 1.7 for complete oxidation.

Orifice Size--

Ursa and Jackson[4] found that the oxygen transfer efficiency of an air-sparged tower was independent of the sparger orifice diameter within the range of 6.4 to 3.7 mm. The sparger used in the tests conducted at RTP consisted of 2.5-cm diam. PVC pipe containing 22, 1.6 mm orifices formed by drilling through the pipe wall. It was expected that the smaller holes might give higher K_La values, and thus better transfer efficiency, by reducing

the size of the bubbles formed. It is evident that the transfer efficiencies obtained at RTP (0.29 and 0.27 with a slurry depth of 5.5 meters) are not significantly different from the values predicted on the basis of Jackson's data for 6.4 mm orifices, shown in Figure 7. It may be concluded, therefore, that the transfer efficiency is not affected by the size of the sparger orifices even when the range is extended to 1.6 mm.

The above conclusion was tested by experiments with a sparger containing 22, 6.4 mm orifices. The results of this test showed 90.9 percent oxidation in the 5.5 m tower at an air stoichiometry of 2.3 and m_g = 2660 g mol/hr(m^2). Assuming 15 percent oxidation in the scrubber, the oxygen transfer efficiency was 0.33, confirming that no loss of oxidation efficiency was incurred by increasing the size of the sparger holes. The scrubbing configuration used in this test was the same as that shown in Figure 13, with a pH of 6.1 in the EHT.

Figure 14 compares the oxygen transfer efficiencies obtained in the RTP pilot plant, using various sparger orifices and tower heights, with the values predicted by Equation (9). The data agree well with the model based on liquid-film diffusion control, within the range of oxidizer heights tested. Since the transfer efficiency is independent of orifice diameter within the range of 1.6 to 6.4 mm, the larger size should be used because of the lower air pressure required for any given air injection rate. Thus, the overall power input for air compression will be minimized.

Chloride--

It was shown above that slurries containing from zero to 14,300 ppm chloride could be oxidized in the two-stage scrubber. Additional tests

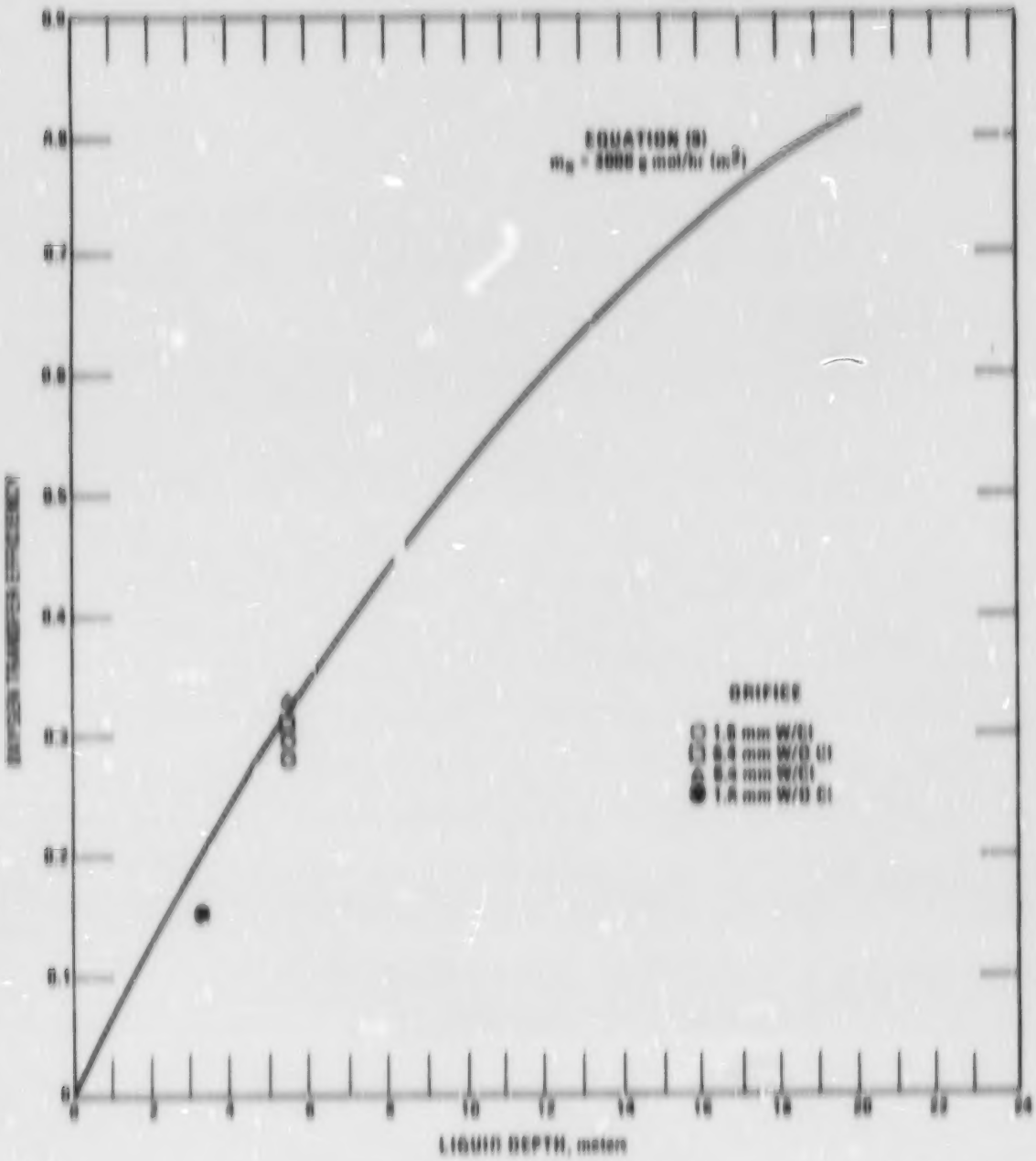

Figure 14. Comparison of O_2 transfer efficiencies obtained in the RTP pilot plant with the liquid film diffusion model at 50°C.

were made with the single-stage scrubber, measuring the O_2 transfer efficiency in the absence of chloride. Using a 3.5-m slurry depth, 6.4 mm orifices, and an air stoichiometry of 2.38, the total oxidation was 87 percent. By Equation (11) the O_2 transfer efficiency was 0.31 which is not significantly different from the efficiencies obtained when chloride was present. Contrary to the results reported by other investigators, that bubble size is influenced by ionic strength, it is concluded from the ISBL-RTP tests that oxidation efficiency will not be affected by chloride (which increases the ionic strength).

Air Ejector Tests

In addition to the air-sparged tower, an air ejector was also tested as a means of aerating the EHT in a single-stage scrubber. The ejector, shown in Figure 15, was a Penberthy model 104A manufactured by Houdaille Industries, Inc. It was made of bronze and was 22 cm long. The ejector was mounted in the side of the EHT near the bottom of the tank. Slurry was pumped through it at a rate of 98 liters/min at an inlet pressure of about 1.4 kg/cm^2. The high velocity of the slurry in the 10.3 mm nozzle aspirated air into the liquid stream. The high shear thus developed in the throat of the ejector broke the air into minute bubbles which were ejected horizontally across the bottom of the EHT and dispersed upward, aerating the slurry in the tank. The main feature of the ejector was its ability to create smaller bubbles than could be obtained with a sparger, resulting in higher transfer factors in accordance with Equation (6). The greater transfer efficiencies thus produced should permit a reduction of tower height and/or a reduction of air stoichiometry.

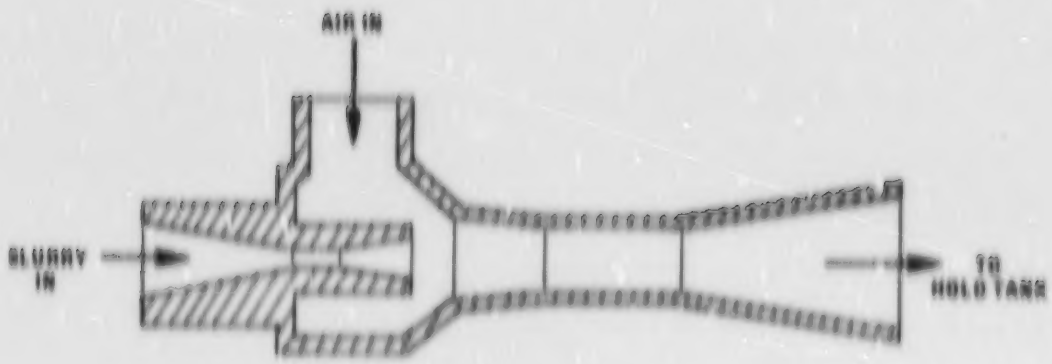

Figure 15. Penberthy air ejector.

The ejector tests were conducted in the manner shown in Figure 16, aerating the EHT (h = 1.1 m) so that oxidation was forced in the slurry recirculating within the scrubbing loop of a single-stage TCA scrubber. As shown by the results summarized in Figure 16, 99% oxidation was obtained at an air stoichiometry of 1.9. As pointed out in the description of the two-stage tests, this same system required an air stoichiometry of 6 to 7 for good oxidation when aerating by air-sparging. The ejector clearly produced a marked improvement in oxygen transfer. Tests of the ejector made with the EHT stirrer turned off (normal stirring speed = 1725 rpm, required an air stoichiometry of 2.7 for complete oxidation, indicating that the stirring contributed to the overall performance of the ejector. These tests also showed that the solids could be maintained in suspension without any mixing other than that provided by the ejector.

Air Feed Pressure--

In addition to the high oxygen transfer factors associated with ejector aeration, which permit efficient oxidation to be achieved in shallow tanks, this approach also has the advantage of a lower air pressure requirement. This derives from the reduced pressure developed by the high velocity of the slurry in the ejector throat, which aspirates air into it. Figure 17 compares the air pressure required for the various methods of injection tested at RTP. It shows that the pressure required by the ejector is significantly lower than that needed for air-sparging at any given air injection rate. One objective of the ejector tests was to reduce the air feed pressure to the range that can be provided by air blowers. Successful tests were made at air feed pressures as low as 0.07 kg/cm^2 (1 psig), which is well within

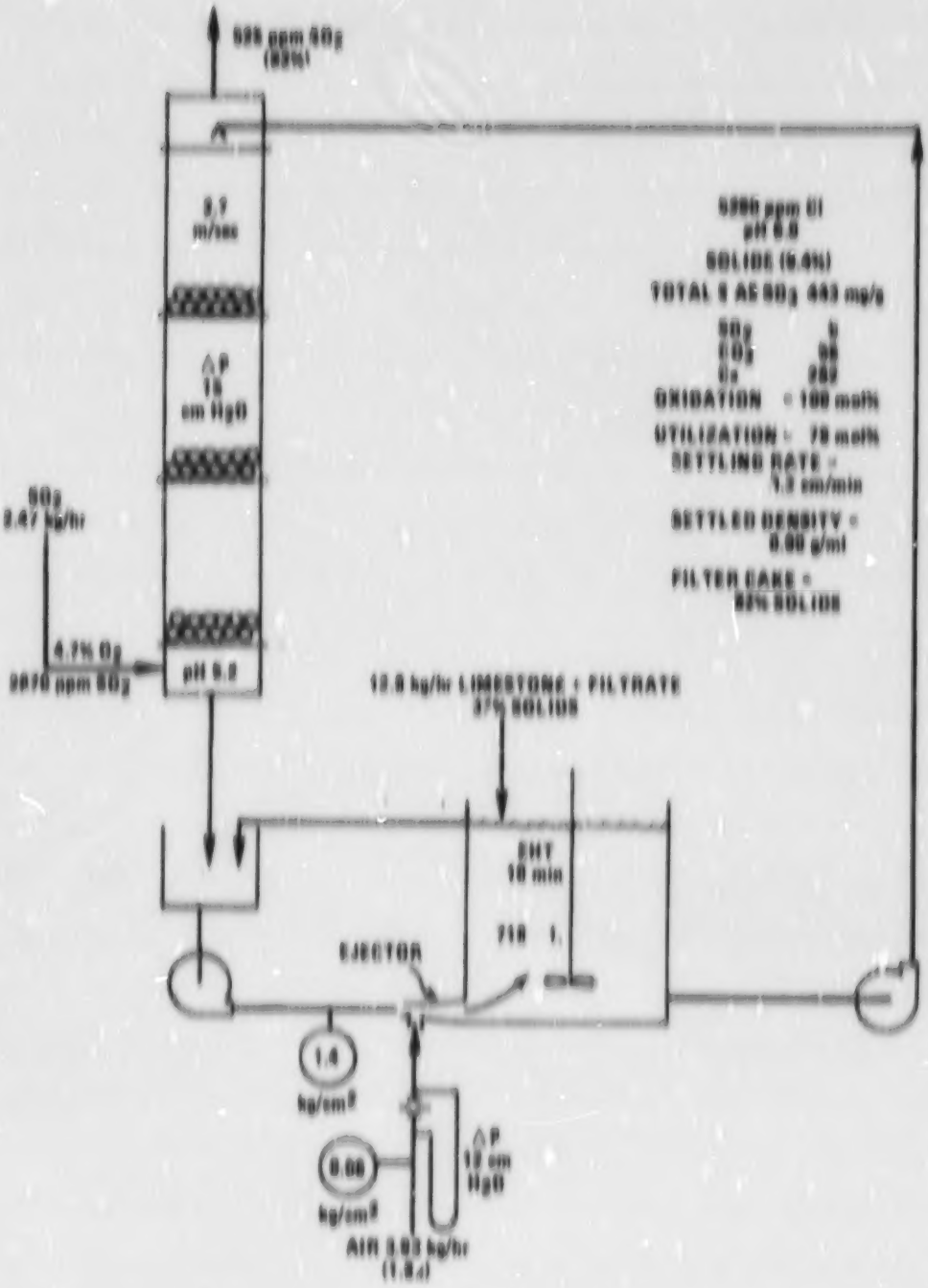

Figure 16. Forced oxidation in single stage scrubber using air ejector to aerate the EHT at pH 6, h = 1.1 m.

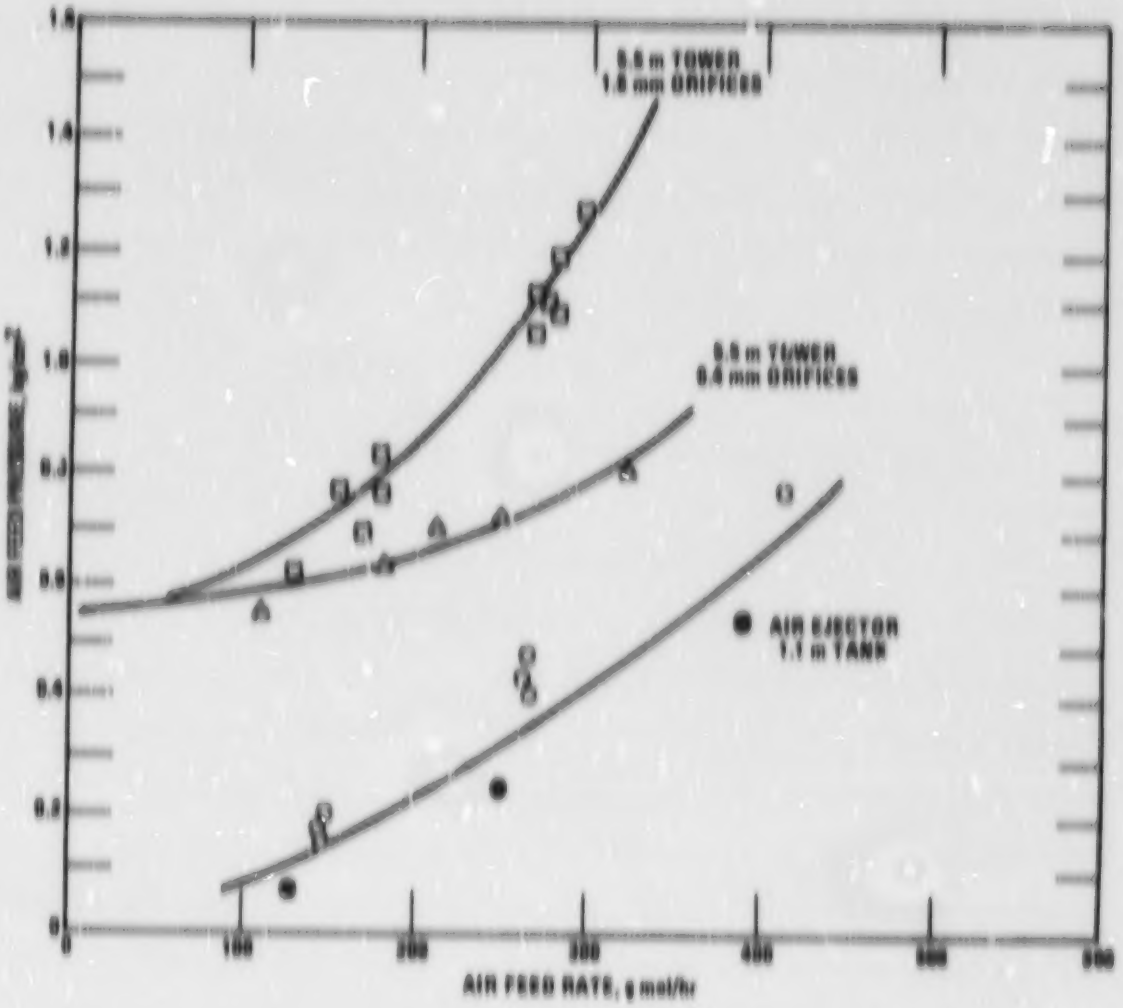

Figure 17. Air feed pressure as a function of air injection rate for air-sparged tower and Penberthy ejector.

that range. Thus, the substitution of an air blower--and a slurry pump--for an air compressor should be feasible in systems employing ejectors.

Most of the tests were conducted with the ejector feed slurry taken from a separate shallow tank located at the bottom of the tower, as shown in Figure 16. This arrangement allowed for the oxidation of some of the SO_2 while it was still concentrated in the liquor coming out of the absorber. Successful tests were also conducted without that tank, with the ejector fed with slurry recycled from the EHT, as shown in Figure 18. The latter configuration required somewhat higher air feed pressures as indicated by the data of Figure 17 (open circles).

Limestone Utilization--

Fouling of the mist eliminators has traditionally been the chief obstacle to good operating reliability of limestone scrubbers. Experience at the EPA/Shawnee Test Facility has shown[7] that the fouling problem is closely related to the level of limestone utilization at which the scrubber is operated; fouling of the mist eliminator does not occur when the utilization is maintained above 85 percent (or the limestone stoichiometry is maintained below 1.18). It is therefore important to determine whether a limestone scrubber, in which oxidation is forced to completion within the scrubber loop, can operate at a limestone utilization of 85 percent or more. Successful tests were made at this level of utilization while operating the RTP scrubber at 98 percent oxidation. One of these tests is summarized in Figure 19; the limestone utilizations calculated from these data are given in Table 1 for each of the three possible methods of measurement.

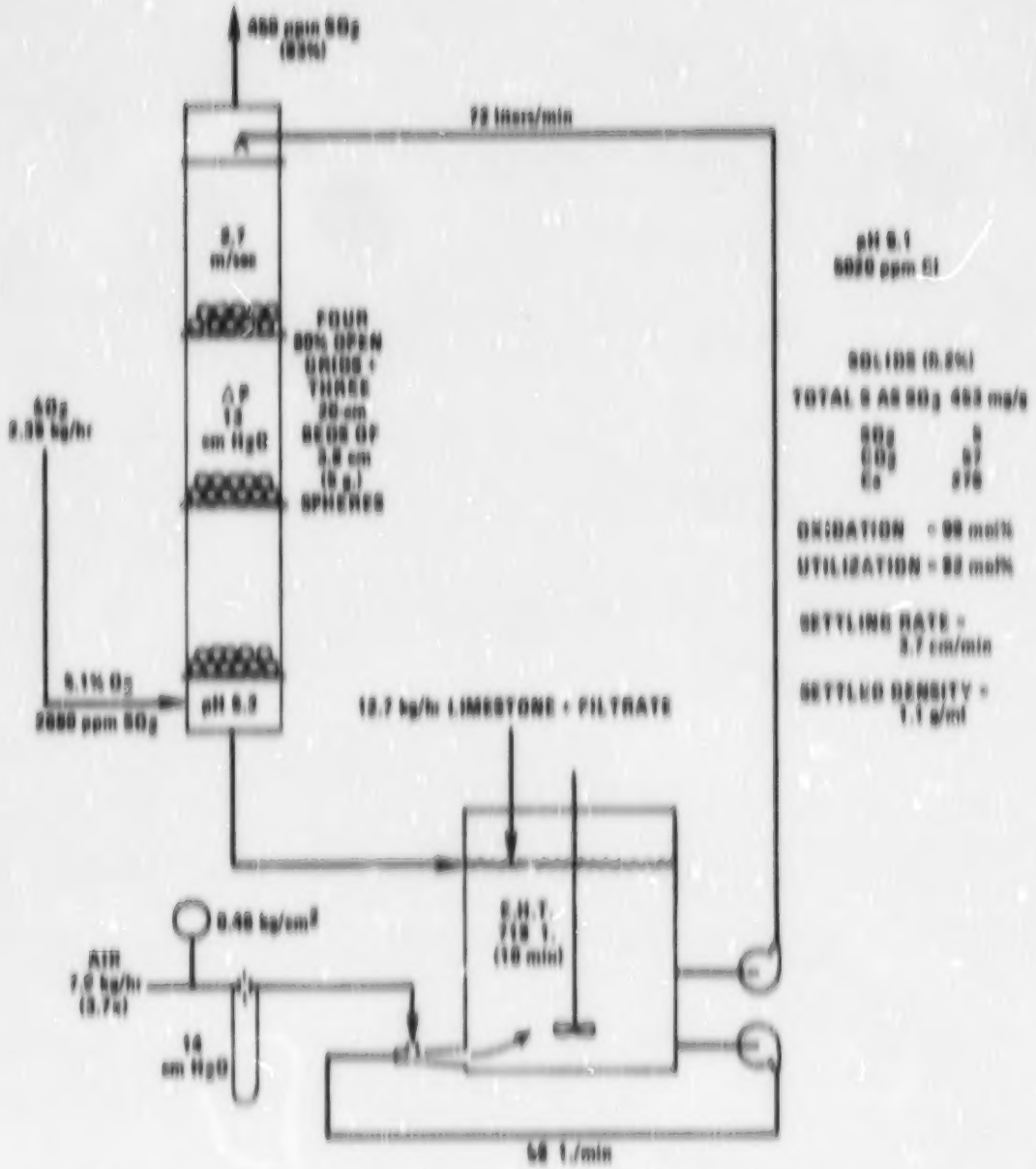

Figure 18. Forced oxidation in single stage scrubber, using ejector to aerate the EHT slurry recycle from EHT.

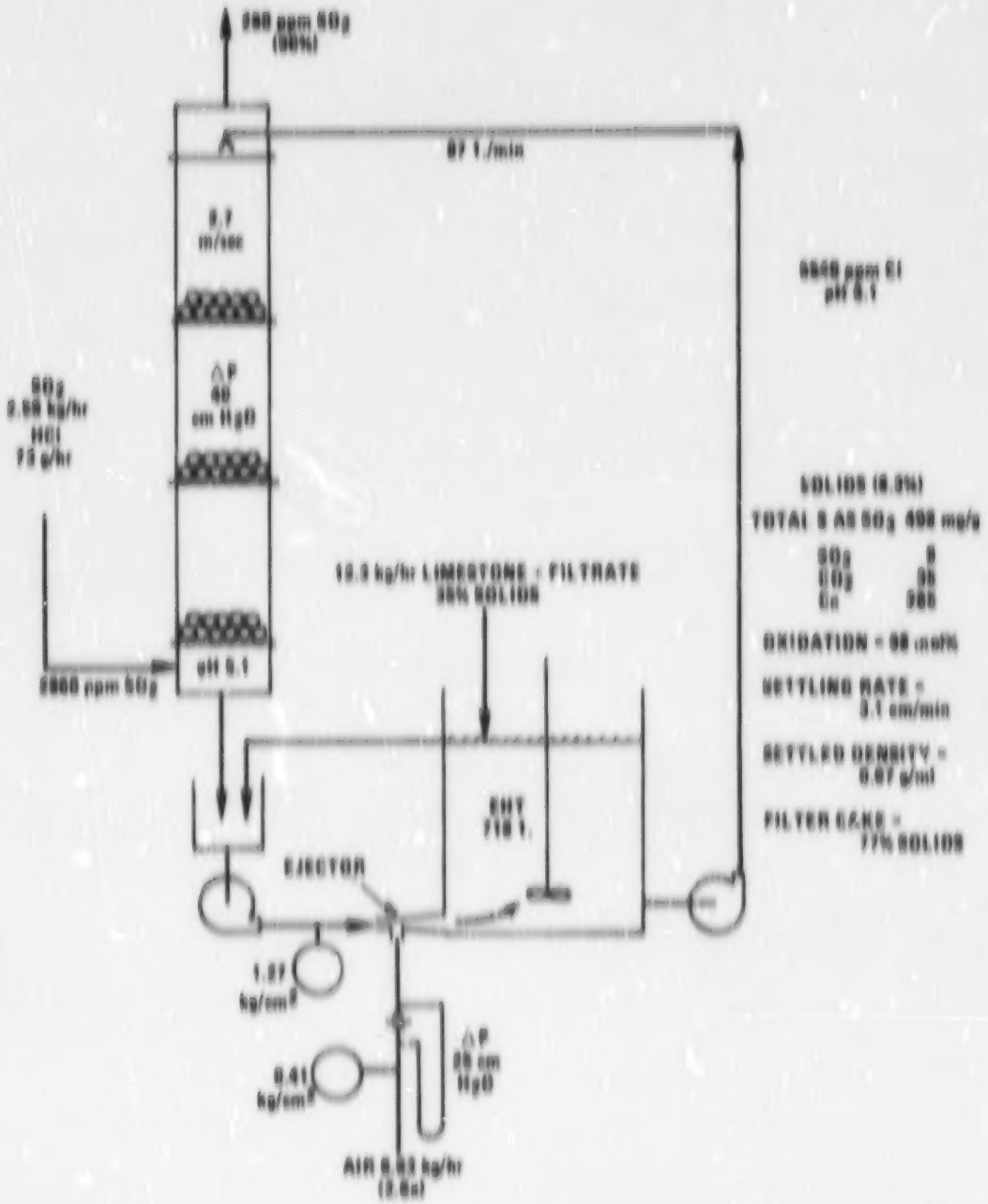

Figure 19. High limestone utilization test.

TABLE 1. LIMESTONE UTILIZATIONS FOR DATA OF FIGURE 19

Basis of Measurement	Utilization, mol percent
Solids S/Ca mol ratio	93
Solids CO_3/Ca mol ratio	88
Scrubber material balance	90

it was concluded that a limestone scrubber can be operated at the utilization levels required for the prevention of mist eliminator problems while forcing oxidation in a single-stage system.

The pH of the aerated slurry in the EHT was higher than the pH's observed without aeration. For example, at 85 percent limestone utilization and with 5000 ppm Cl^- in the scrubbing liquor, a pH of 5.6 would be expected when operating without forced oxidation, based on experience at both the Shawnee Test Facility and the RTP pilot plant. As indicated in Figure 19 pH's of 6 were consistently obtained when forcing oxidation at utilizations up to 90 percent. The main factor influencing the scrubber feed pH during these tests was not limestone utilization, but air stoichiometry. The pH increased with the air injection rate, to values as high as 6.6 at an air stoichiometry of 5.

No scaling of the tower occurred during any of the forced oxidation tests with the single-stage scrubber, which were conducted during 4 months of operation. Normal test conditions for the scrubber were L/G = 9.8 liters/m^3, EHT residence time = 10 min, and slurry solids = 8 percent without fly ash. Average $CaSO_4 \cdot 2H_2O$ saturations of the scrubber feed liquor, as determined by chemical analysis, are shown in Table 2.

TABLE 2. $CaSO_4 \cdot 2H_2O$ SATURATION OF SCRUBBER FEED LIQUOR: SINGLE-STAGE SCRUBBING WITH FORCED OXIDATION

Constituent	Concentration, ppm				
	Nov 1-5	Nov 8-12	Nov 15-19	Nov 22-24	Dec 6-10
Ca	2480	2630	2510	2180	2130
Mg	474	545	662	741	806
SO_3	13	169	0	39	113
SO_4	1504	1404	1520	1651	1626
CO_3	89	106	106	93	119
Cl	4790	5200	5440	4750	5550
pH	6.0	5.8	6.2	6.1	6.1
Ion balance[a], % error	-2.9	-2.2	-3.6	-0.2	-6.7
$CaSO_4 \cdot 2H_2O$ Saturation[a], %	103.3	95.2	96.0	95.2	92.6

Within the accuracy of the sampling and analytical methods used, the scrubber feed liquor had no significant supersaturation with respect to dissolved gypsum at 50°C. Saturation tests at 25°C showed relative saturations in the range of 1.1 to 1.2, which agrees with the analytical data when corrected for temperature; i.e., about 1.0 saturation. The absence of supersaturation is attributed to the high concentration of pure gypsum seed crystals in the EHT slurry when oxidation is forced to completion. It is interesting to compare these values with the saturation level that would be expected on the basis of measurements of the crystallization rate of pure gypsum, which is[8]:

$$CaSO_4 \cdot 2H_2O \text{ crystallization rate (g mol/min)} = m\,(r-1)^{2.1} \times 10^9\, e^{-19{,}000/RT} \qquad (14)$$

[a]Calculated with Bechtel-Modified Radian Equilibrium Program at 50°C.

where m = the total grams of $CaSO_4 \cdot 2H_2O$ (dry solid) present in the EHT, r = the relative saturation of dissolved gypsum in the liquor, R = 1.98 cal/g mol °K, and T = temperature, °K. At the operating conditions used in the RTP tests, the crystallization rate (= SO_2 absorption rate x oxidation) is:

$$\frac{2600\ (0.85)\ 0.97}{(64.1)\ 60} = 0.555 \text{ g mol/min}$$

and the total gypsum crystals present in the EHT (at 8 percent solids and 718 liters volume) is:

$$80\ (718) = 57{,}400 \text{ grams } CaSO_4 \cdot 2H_2O$$

which, with Equation (13), gives:

relative saturation = 1.04 at 50°C

Thus the observed saturation levels are in agreement with the values expected on the basis of laboratory measurements of the crystallization rate of gypsum. It was concluded from these tests that forced oxidation can be conducted within the scrubber loop of the single-stage scrubber at pH 6 without scaling. The difference between this result and the less favorable result obtained with the two-stage system at pH 6 is attributed primarily to the higher liquid-to-gas ratio at which the single-stage scrubber operates.

PROPERTIES OF OXIDIZED SLURRY

The physical properties of the oxidized slurries obtained with the single-stage scrubber operating at pH 6 were similar to those obtained with the two-stage scrubber operating at pH 4.5. These properties, which were reported at the 1975 FGD symposium in New Orleans[1], were 2 to 3 cm/min settling rate and 0.9 to 1.0 g/ml settled (dry bulk) density. Compared to sulfite slurries this represents an improvement by a factor of 10 in settling rate and a factor of 2 in density. As a result of the greater sludge density,

the volume is also reduced by about 30 percent. Most importantly, however, the oxidized slurry was filterable to 80 percent solids compared to 62 percent solids normally obtained with sulfite slurries at RTP; the sulfite slurries produced at Shawnee have generally been even less filterable, averaging only 50 percent solids. The filterability of the solids obtained with the single-stage system were generally better than that obtained with two stages--a result that may be associated with the longer particle retention times in the larger EHT of the single-stage system.

Attempts to conduct the oxidation outside the scrubber loop (slipstream aeration) showed that higher air stoichiometries were necessary to complete the oxidation. Using the Penberthy ejector to aerate a tank of the same volume (710 liters) as that used for the EHT in the single stage oxidation tests yielded only 70 percent oxidation at 3.5 air stoichiometry when tested in the slipstream mode. Figure 20 shows the scrubber configuration for this test. The oxidation rate in this case was only 0.35×10^{-3} g mol/l.(min), which suggests that the dissolution of the solid $CaSO_3$ may be the limiting factor. In this situation all of the SO_2 absorbed in the scrubber must be redissolved at high pH, which is not the case when oxidation is conducted within the scrubbing loop. By increasing the air stoichiometry to 5.4, 96 percent oxidation was obtained in the slipstream. The properties of the gypsum thus produced, however, were interior to those obtained by oxidation within the scrubbing loop. It was concluded from these results that forced oxidation must be conducted within the scrubbing loop in order to obtain the best-settling, most filterable sludge with the least amount of air injected.

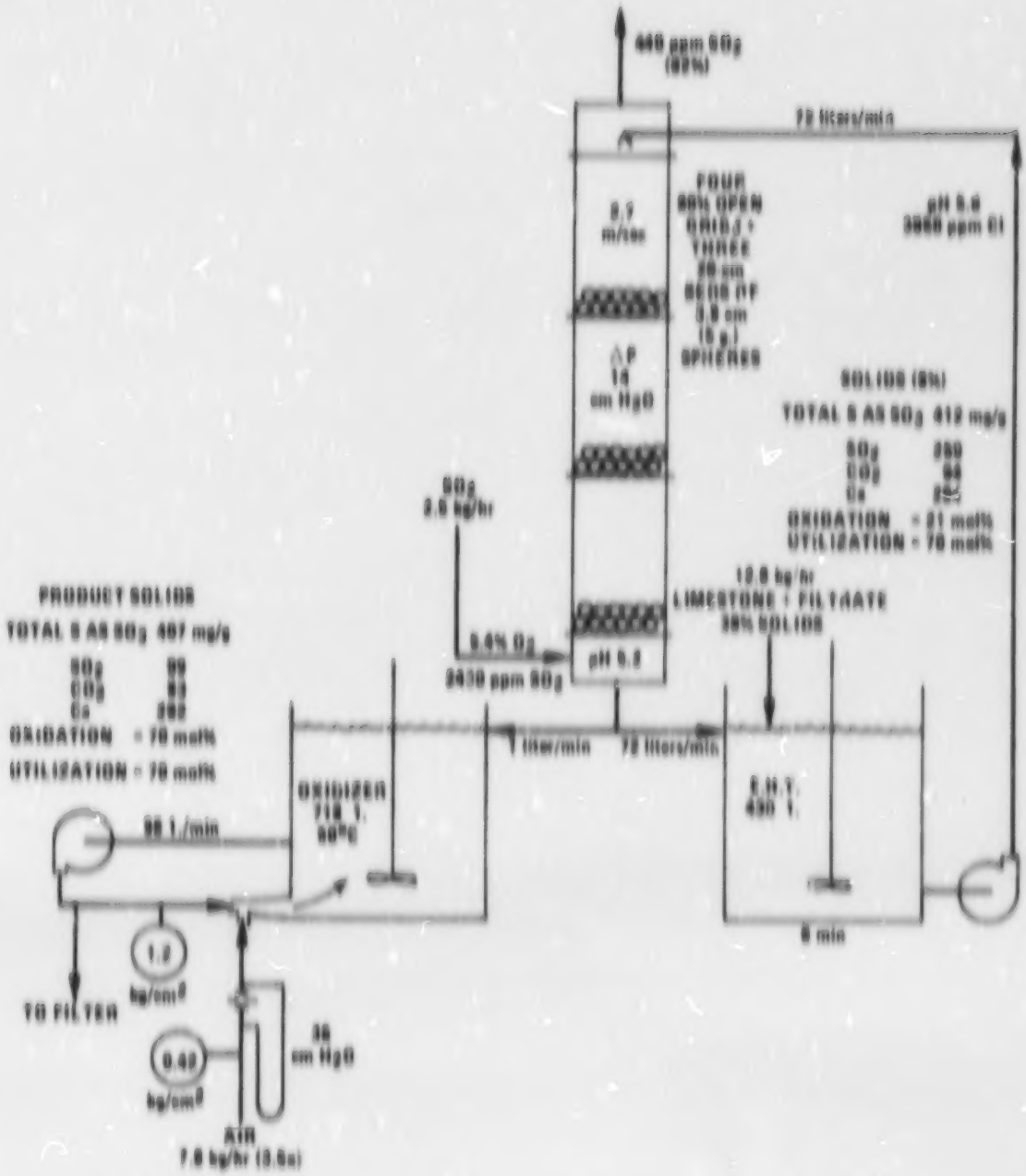

Figure 20. Slip stream oxidation test.

SECTION 7

DISCUSSION OF RESULTS

The most important result of these experiments is the attainment of 80 percent solids in the filter cake when oxidation is forced from calcium sulfite to gypsum. This degree of dewatering has been demonstrated in the pilot plant with both single-stage and two-stage scrubbing configurations. A final sludge dryness of 80 percent solids is important because it is expected to meet the minimum requirement for direct disposal as landfill. It therefore opens the possibility that chemical fixation of the sludge may be avoided. The disposal of dry fly ash at the same site will further increase the dryness of the sludge to 87 percent solids--considerably higher than can be achieved by any other method, and well within the requirements for stable landfill of optimum compaction characteristics.

On the basis of IERL-RTP results with single-stage and two-stage oxidation, Table 3 projects the effect of the improved dewatering properties of the sludge upon the total waste production in a 1000-MW power plant (3.5 percent sulfur and 13 percent ash). It shows that a potential reduction of 47 percent is possible in the total waste produced by the power plant when forced oxidation is employed. The base case for this comparison represents current practice as defined in the SOTSEP report[9]. Another factor that is sometimes overlooked is that forced oxidation also reduces the volume of the sludge, in addition to reducing the total tons produced per hour. In our experience this reduction in volume amounts to about 30 percent.

TABLE 3. ANNUAL WASTE SLUDGE PRODUCTION BY A 1000-MW COAL-FIRED[a] POWER PLANT EQUIPPED WITH LIMESTONE FGD SCRUBBERS

(SHORT TONS)

Fly Ash Collection	Wet		Dry	
Dewatering Procedure	Settling		Oxidation/Filtration	
Limestone Utilization, mol %	60	63	80	95
Oxidation, mol %	10	10	97	97
Coal Ash, Dry	338,000	338,000	338,000	338,000
$CaSO_3 \cdot 1/2\ H_2O$	322,000	322,000	7,200	7,200
$CaSO_4 \cdot 2H_2O$	48,000	48,000	463,000	463,000
$CaCO_3$	185,000	185,000	69,000	14,600
Solids Moisture, %	50	50	20	20
Total Wet Sludge	1,790,000	1,110,000	673,800	606,000
Total Waste	1,790,000	1,448,000	1,011,800	944,000
Reduction of Waste Compared to Base Case, %	Base Case[b]	19	44	47
Final Sludge[c] Density, % Solids	50	63	87	87

[a]Coal = 12% ash, 3.5% sulfur

[b]SOTSEP Report[9], p. 60.

[c]Dry fly ash blended with wet sludge

The importance of pH as a variable influencing forced oxidation is evidently much less than previously supposed. The results of IERL-RTP tests with the two-stage scrubber at oxidizer pH's of 4.5 and 6 did not show a significant difference within the accuracy of the measurements of oxidation rate. Nor was the performance of the two-stage system at low pH superior to the oxidation efficiency obtained in the single-stage system at high pH. The argument that low pH might provide better performance if the tests were made with more efficient aerators having a greater transfer factor is refuted by the single-stage test results. The single-stage tests show conclusively that the oxidation rates measured in the laboratory--and confirmed in the RTP pilot plant--are great enough even at pH 6 to accomplish complete oxidation in systems of current design without catalyst addition. The only apparent constraint is that the physical resistance to oxygen absorption must be overcome, either by using large amounts of excess air or by providing for efficient oxygen transfer in the oxidizer. In the latter case, the RTP tests have shown that the transfer efficiencies needed for realistic air stoichiometries can be obtained with air-sparged towers of 5.5 mete/s depth or greater, or by the use of air ejectors. Once adequate O_2 transfer efficiency has been designed into the system, pH's lower than 6 are simply unnecessary for good oxidation.

The advantages of conducting forced oxidation at pH 6 instead of pH 4.5 are very clear. First, it will permit the conversion to be carried out in the simplest possible scrubbing configuration--a single stage system, without the addition of extra tanks, absorbers, or chemicals. Oxidation can thus be conducted in scrubbers of current design that are already in operation. Secondly, it means great simplification of the control requirements, since

the feed rates do not have to be controlled in two independent reactors--one at low pH for oxidation and the other at high pH for good SO_2 removal. Thirdly, and probably the most important, is the neutral pH of the sludge produced when oxidation is conducted in a single-stage scrubber. Sludge produced at pH 4.5 probably cannot be used as landfill without additional treatment to raise the pH. Finally, RTP results seem to indicate that somewhat better physical properties are obtained when the sludge is oxidized in a single-stage scrubber. This is not unreasonable, considering the difference in particle retention times characteristic of single stage and two stage systems: gypsum crystals are retained about 15 hours in the EHT of a single-stage scrubber operating at 3000 ppm inlet SO_2, but only 5 hours in the first stage of a two-stage system operating with the same 10-min EHT residence time in the first stage. Thus, the gypsum crystals are in contact with the super-saturated liquor for a longer period of time in a single-stage system and should grow to a larger average size.

The technique of forced oxidation used in Japan, which is based on low pH--even to the extent of adding H_2SO_4 in large amounts--is somewhat baffling in view of the RTP results. It is especially so considering the high efficiency aeration that is obtained with the JECCO spinning-cup air atomiser. A possible explanation of the poor performance reported for those systems at pH's greater than 5 may be that the $CaSO_3$ solid dissolution plays the dominant role in the performance of the oxidiser when the aeration is conducted outside the scrubbing loop. The observed loss in "oxidation rate" may actually have been caused by low dissolution rate of the $CaSO_3$ at high pH. The tests with slipstream oxidation tend to support such an interpretation in that the

apparent rate of oxidation tended to be lower than those observed when oxidation was conducted in the EHT. The potential limitation of the solid dissolution step is avoided when oxidation is forced with/n the scrubbing loop, because the $CaSO_3$ is exposed to low pH when it is recirculated through the scrubber.

The conclusion that oxygen transfer is the controlling factor when oxidation is carried out in the scrubbing loop appears to be well established by the IERL-RTP results. The conclusion was tentatively drawn earlier[1] on the basis of the observed effect of oxidizer height on the air stoichiometry required for complete oxidation in the two-stage scrubber. The conclusion is verified by three additional observations reported here: 1) oxidizer recycle influences the bubble residence time, and thus the oxygen transfer efficiency, by prolonging the contact between air and liquid; 2) the absence of any strong effect of pH on oxidation efficiency indicates that the oxidation reaction is fast once the oxygen gets into the solution (i.e., the chemical reaction rate is not an important resistance); and 3) the very large effect of interfacial area seen with the ejector tests at high pH confirms the importance of oxygen diffusion as the controlling factor in the overall oxidation process.

The conclusion that oxygen transfer is the controlling resistance is especially important because the underlying mechanism of that process--liquid film diffusion--is the same as that which governs the process of waste water aeration. The technology for waste water treatment has been developed over a long period of time and is well understood in terms of design criteria for large scale equipment. Thus, those same criteria should be directly applicable

to the design of FGD oxidation systems. The work of Jackson in this area[4,5] is probably the most comprehensive and the most useful for this purpose, and has been used in this report as a basis for evaluating the RTP results. It is clear that the equation for oxygen transfer derived by Jackson (Equation 4) predicts the performance of the RTP oxidizer within the accuracy of the measured transfer efficiencies. It can therefore be assumed valid for $CaSO_3$ slurries as well as for the clear sodium sulfite solutions with which Jackson worked. The significance of this conclusion is that it should be possible to design air-sparged towers for FGD systems with considerable confidence. It is interesting that one of Jackson's conclusions is that the amount of oxygen that can be transferred per unit of energy expended can be increased by the use of deeper aeration tanks. Although energy efficiencies of 0.75 to 1.5 kg of O_2/kwh are characteristic of current commercial aerators (h ≤ 4 m), Jackson estimates[4] that an efficiency of 8.7 kg of O_2/kwh should be possible at h = 16 m. For this reason large scale scrubber tests of a combination EHT/oxidizer of this depth should be undertaken.

The results also indicate that the use of an air ejector(s) in a shallow tank would be an alternative approach, especially applicable to systems that are already in operation. It would require only the installation of the ejector(s) in the hold tank and the installation of a second slurry pump to recirculate slurry through the ejector. Although a second pump is required, IERL-RTP tests indicate that it can probably replace the air compressor that would be needed for a tower. (An oxidation tower would not necessarily need two pumps, since the hydrostatic head in the EHT/oxidizer would be sufficient

to feed the slurry to the scrubber.) The main question regarding the use of ejectors is the effect of scale up: whereas the performance of a sparged tower is predictable for larger units, the performance of larger ejectors is not. The shear developed in the throat, and other factors that affect the size of the bubbles produced are not constant as the throat size is increased and can result in poorer performance of larger units[10]. Unless small ejectors are used in multiple units, this approach should not be attempted on full scale FGD systems until a larger ejector has been tested in the Shawnee scrubber. Such tests will be made in 1977.

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